

Editor's Preface

I am proud to bring to you, as the first volume under my editorship of this series, a treatise of enormous value and broad scope.

It has never been more true than today that the more we learn about the composition of matter, of the environment, and of biological systems, the more we will understand how chemistry controls function. It has become evident that trace and ultratrace analysis remain challenging, and that without a proper and deep understanding of each step in a method, it is possible to be in error. A thorough reading of the first two sections of this volume, and selected reading in the third section, prepare the chemist in all aspects of modern inorganic trace and ultratrace analysis for metals and metalloids. Indeed, the book has pedagogical value. Rarely do modern instrumental analysis texts venture in any depth beyond the physics surrounding the actual measurement.

The information in this volume on sample preparation, and on selected metal determinations, is a boon to the industrial, government, or academic chemist with teaching or training responsibility.

S.G. Weber

Authors' Preface

The development of trace inorganic analysis is a response by analytical chemists to the increasing concerns about the role of elements at low concentrations in the environment, biology, medicine, industrial quality control and other fields. Whereas classical analysis has dealt with sample components exceeding the 0.01% concentration level, for trace analysis those at levels between 0.1 and 100 $\mu\text{g g}^{-1}$ (ppm) are interesting. The determination of concentrations below 0.1 $\mu\text{g g}^{-1}$ is termed extreme trace (ultratrace) analysis.

The increasing requirements in terms of sensitivity, sample throughput, precision and accuracy of analysis are driving the development of novel and more effective analytical techniques. The most important group are spectrometric techniques which only in few cases can be matched by electrochemical methods. Spectrometric techniques are based on a correlation of the intensity of an element-specific signal observed in an electromagnetic or mass spectrum with the concentration of the element in the sample. They are divided according to the origin (and wavelength) of the spectrum used for quantification into molecular or atomic absorption, emission and fluorescence spectrometry, X-ray fluorescence, α -, β -, and γ -spectrometry and mass spectrometry. Further subdivisions are often made according to how the spectrum is generated (atomization, excitation or activation). The most important spectrometric techniques include atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and mass spectrometry (MS); the latter two are usually associated with excitation in an inductively coupled plasma (ICP). Their rapid development contributed to a decline of the role of spectrophotometry and X-ray fluorescence (XRF) in trace analysis in recent years (insufficient sensitivity) and neutron activation analysis (the need of access to a nuclear reactor).

It must be emphasized that, except for some sophisticated instrumental techniques, the lower concentration levels in real samples are not accessible but are after the sample decomposition and/or a chemical separation/preconcentration of the analytes from the matrix prior to measurement. More or less complex spectrochemical procedures are still dominant in the majority of academic, industrial and commercial analytical laboratories and enjoy a unique and widely recognized role in the certification of candidate reference materials and secondary laboratory standards. A deep understanding of these methods is a prerequisite of successful analysis. In particular this applies to the awareness of contamination risk which is omnipresent in trace and ultratrace analysis.

This book discusses analytical methods that combine a chemical sample treatment step (e.g. decomposition, separation and preconcentration, matrix modification) with a spectrometric technique, applied to the determination of metals and metalloids (As, B, Sb, Se, Si and Te) at trace and ultratrace levels. Analytical techniques for surface analysis or for direct bulk analysis (e.g. instrumental activation analysis, XRF, ablation MS techniques) are not included unless preceded by a chemical sample processing step. In principle, the book covers analytical chemistry of stable nuclides only, but some important long-lived naturally occurring isotopes (U, Th, Tc) and anthropogenic environmental contaminants ($^{239,240}\text{Pu}$, ^{247}Np) have been included. Particular attention is given to the analysis for the chemical species in which the element is present in the analyzed material (speciation).

The overview of current spectrochemical techniques used in elemental trace analysis should enable an analyst, facing the task of analyzing a sample type that he or she has never analyzed before, to reach a decision which instrumental technique to choose and how to handle the sample starting from sampling and decomposition, through separation and preconcentration, until the final determination step. A thorough critical survey of the literature for the last ten years (1985–1994) specifies analytical characteristics likely to be achieved and gives references to source articles in peer-reviewed journals.

The book is composed of three parts: general principles and characteristics of analytical methodologies (Part I), practical issues of sample treatment and multielement analysis (Part II) and determination of individual elements (Part III). Part I discusses general aspects of successive steps of an analytical procedure from sampling and sample decomposition (acid attack, fusion, decomposition in gas streams) in

simple and assisted (microwave, ultrasonic, pressure) systems, through separation and preconcentration (extraction, volatilization, coprecipitation, sorption and chromatographic techniques) to instrumental determination techniques (spectrophotometry and spectrofluorimetry, atomic absorption, emission and fluorescence, X-ray, nuclear and mass spectrometric techniques). Emphasis is placed on automated sample processing — flow injection analysis (FIA) and the rapidly developing field of analytical chemistry of metal and metalloid moieties (speciation and hyphenated techniques). The last chapter of Part I, devoted to accuracy in trace analysis, discusses various quantification techniques, sources of errors and the role of certified reference materials (CRMs) for method validation. The chief objective of Part I is to present principles, analytical characteristics and possible interferences of modern spectrochemical techniques and to direct the reader to relevant monographs, edited works, topic and tutorial reviews, written by leading experts in the related fields. Part I should give the reader a global view on modern analytical spectrochemistry and enable him or her to establish the relevance and suitability of a given analytical method for the analytical task to be solved, and to estimate its chance of success.

Part II is devoted to practical aspects of initial sample handling and multielement trace analyses of different types of real samples: environmental, geological, biological and clinical, and inorganic and organic industrial materials. Both the cases of direct analysis following a chemical sample decomposition and those involving multielement separation and preconcentration using extraction, hydride generation and sorption are discussed. Each chapter contains several tables summarizing procedures for multielement analysis of real samples and certified reference materials available for method validation.

Part III contains 54 alphabetically arranged monographic reviews on spectrochemical trace analysis for individual elements. Each chapter gives basic information on analytico-chemical properties of the element which is followed by an overview of methods for its separation, preconcentration, and instrumental detection. Particular attention is given to practical issues, difficulties and quality assurance during the analysis of real samples. Each chapter contains tables summarizing the key steps of the procedures developed for the trace element determination and the detection characteristics reported.

The book contains *ca* 5000 carefully selected references, in general not older than 1985. Strong preference is given to full papers in peer-reviewed English-language journals, but for elements which are pertinent

in geochemistry, environmental or biomedical fields a number of references from specialized field-related journals are given. In our opinion, these references together with those cited therein give a sufficiently extensive coverage of the topic. For a more comprehensive survey, the reader is advised to consult the periodic reviews in *Analytical Chemistry* and *Journal of Analytical Atomic Spectrometry* which were not cited anywhere in the book.

Ryszard Łobiński
Zygmunt Marczenko

List of abbreviations

AAS	atomic absorption spectrometry
ADL	absolute detection limit
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
APDC	ammonium pyrrolidinedithiocarbamate
ASV	anodic stripping voltammetry
BPHA	<i>n</i> -benzoyl- <i>n</i> -phenylhydroxylamine
5-Br-PADAP	2-(5-Br-2-pyridylazo)-5-diethylaminophenol
CF	continuous flow
CCP	capacitively coupled plasma
CGC	capillary gas chromatography
copptn.	coprecipitation
conc.	concentrated
CP	cetylpyridinium ion (or its salt)
CTA	cetyltrimethylammonium ion (or its salt)
CV	cold vapour
DAM	diantipyrylpropylmethane
DBDTC	dibenzylthiocarbamate
DBA DBDC	dibenzylammonium dibenzylthiocarbamate
DCP	direct current plasma
DDTC	diethylthiocarbamate
DEE	diethyl ether
detn.	detection
dil.	diluted
diln.	dilution
dissoln.	dissolution
DIPE	diisopropyl ether
DL	detection limit
DMF	dimethylformamide
DMSO	dimethylsulphoxide
DTC	dithiocarbamate
DTPA	dithiophosphoric acid

ED	energy dispersive
EDL	electrodeless discharge lamp
EDTA	ethylenediaminetetraacetic acid (di-Na salt)
EGTA	ethyleneglycolbis(2-aminoethyl ether- <i>N,N,N',N'</i> -tetraacetic acid)
EI	electron ionization
eln.	elution
ETA	electrothermal atomization
ETV	electrothermal vaporization
evapn.	evaporation
extrn.	extraction
FAAS	flame atomic absorption spectrometry
FAB	fast atom bombardment
FAES	flame atomic emission spectrometry
FI	flow injection
FIA	flow injection analysis
FLU	spectrofluorimetry
FPD	flame photometric detection
GC	gas chromatography
GD	glow discharge
GF	graphite furnace
HCL	hollow cathode lamp
HDEHP	di(2-ethylhexyl)phosphoric acid
HMA HMDTC	hexamethyleneammonium hexamethylenedithiocarbamate
HPLC	high performance liquid chromatography
HR	high resolution
ICP	inductively coupled plasma
ID	isotope dilution
INAA	instrumental neutron activation analysis
LEI	laser-enhanced ionization
LA	laser ablation
LC	liquid chromatography
LI	laser induced
LTA	low temperature ashing
MIBK	methyl isobutyl ketone
MIP	microwave-induced plasma
MS	mass spectrometry
MT	metallothionein
NAA	neutron activation analysis
ND	non-dispersive
NTA	nitrioloacetic acid
oxidn.	oxidation
oxine	8-hydroxyquinoline, 8-quinolinol
PAN	1-(2-pyridylazo)-2-naphthol
PAR	4-(2-pyridylazo)resorcinol
PVC	polyvinyl chloride
PDA	photodiode array

PE	polyethylene
PGM	platinum group metals
phen	phenanthroline
pptn.	precipitation
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PIXE	proton-induced X-ray emission
QF	quartz furnace
redn.	reduction
REE	rare earth elements
RF	radiofrequency
RI	resonance ionization
RNAA	radiochemical neutron activation analysis
sepn.	separation
SFC	size-exclusion chromatography
SIM	single ion monitoring
SPE	solid phase extraction
STPF	stabilized temperature platform furnace
TE	transuranium elements
TI	thermal ionization
T-i-OA	tri- <i>i</i> -octylamine
TMDTC	tetramethylenedithiocarbamate
TOA	tri- <i>n</i> -octylamine
TOF	time of flight
TOMA	trioctylmethylammonium
TOPO	tri- <i>n</i> -octylphosphine oxide
TPA	tetraphenylarsonium
TPAO	tetraphenylarsonium oxide
TPP	triphenylphosphine
TPPO	triphenylphosphine oxide
Tris	tris(hydroxymethyl)aminomethane
TTA	2-thienoyltrifluoroacetone
TXRF	total reflection X-ray fluorescence
VIS	spectrophotometry (photometry) in the visible range
volatn.	volatilization
WD	wavelength-dispersive
XRF	X-ray fluorescence
ZAAS	Zeeman atomic absorption spectrometry

Sampling

According to IUPAC, a sample is defined as a portion of material selected from a larger quantity of material [1]. Sampling is defined as the total of activities which end with the acquisition of the test portion (actual subject of analysis). Sampling starts by taking an increment (an individual portion of material collected by a single operation of a sampling device). The collection of one or more increments or units initially taken from a population represents a primary sample which on division and reduction gives rise to a reduced sample of a mass approximating that of the final laboratory sample. The laboratory sample is the one the analyst has the first contact with. The final stage of sampling consists of the selection, removal and preparation of analytical portions from the laboratory sample and is usually performed in the analytical laboratory. IUPAC recommends that the term “sample” should not be used after analytical operations on a homogeneous test portion have begun.

A prerequisite for a test (analytical) sample is its being homogeneous. The homogeneity (heterogeneity) denotes the degree to which a constituent is uniformly distributed throughout a quantity of material. A material may be homogeneous with respect to one analyte or property but heterogeneous with respect to another. The degree of heterogeneity is the determining factor of sampling error. Homogeneity may be considered to have been achieved when the sampling error of the processed portion is negligible compared to the total error of the measurement system [1].

Meaningful analytical results can only be achieved if the test sample is representative, i.e. adequately represents the population of material from which it was drawn. A statistical sampling plan (a predetermined procedure for the selection, withdrawal, preservation, transportation and preparation of the portions to be removed from a population as samples) is intended to minimize the difference between the properties

as estimated from a sample and the actual properties of the lot, within practical constraints. Precautions necessary to avoid changing the characteristics of the sample (contamination, moisture loss or gain) should be considered during sample collection and storage.

Sampling should be considered as an integral step of chemical analysis. Many errors (especially contamination [2]) are committed at this stage and often remain undetected as the analytical chemist is not involved in either the design or the implementation phase of sampling. The analyst must have a perception of the uncertainty involved in sampling as often the analytical methodology is not the limiting factor. Unless the history of the sample is known the analyst is advised not to spend his or her time analysing it. The theory and practice of sampling have been extensively discussed [1–7]. Practical considerations regarding particular sample types are discussed in Part II.

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Decomposition/dissolution techniques

Despite the increasing popularity of direct analytical methods, the dissolution of a sample is still an integral part of most procedures and is mandatory if separation/preconcentration techniques are used. The three basic groups of decomposition methods include acid attack, fusion and decomposition in gas streams. They are usually applied to powder samples (finer than 100 mesh) for the sake of speed. The decomposition methods are undergoing continuous evolution mostly in terms of vessel design and heat transfer which aims at improving the speed and completeness of the process and have been extensively reviewed [1–7].

2.1 ACID ATTACK

Attack with strong inorganic acids (HCl , HNO_3 , HClO_4 and H_2SO_4) and others (H_3PO_4 and HF) is a common method for the dissolution of metals, alloys, geochemical samples and organic materials. Mineral acids are easy to purify, quick to dispense and, apart from H_2SO_4 , do not produce large matrix effects. The choice of the acid depends on the sample composition but also on the separation method and instrumental techniques to be used. Two- or three-component acidic mixtures are preferred rather than a single acid. Ultrapure acids are recognized for trace element analysis.

2.1.1 Acids

The physicochemical properties of the most commonly used acids and the compatible vessel materials are summarized in Table 2.1.

TABLE 2.1

Physicochemical properties of acids used in trace analysis

Acid	Concentration		Density (g ml ⁻¹)	Boiling point (°C)*	Redox properties	Labware allowed	Safety considerations
	(%)	(M)					
HCl	36	6.8	1.18	110 (20.24)	reductor when hot	glass, quartz, PTFE, PP/HTPE (60°C), glassy carbon, Pt, Ta	to be handled in a well-ventilated hood
HF	48	29	1.15	112 (38.3)	none	PTFE, PP/HTPE (60°C), glassy carbon, Pt	gloves necessary
HNO ₃	70	16	1.42	83 120 (68)	oxidant when concentrated (> 2 M)	glass, quartz, PTFE, glassy carbon, Pt, Ta	prone to explosion in a closed vessel
H ₂ SO ₄	98	18	1.84	338 (98.3)	oxidant when hot and concentrated	PTFE (250°C), glass, quartz, glassy carbon, Pt, Ta	
H ₃ PO ₄	85	15	1.7	213 (decomposes)	none	PTFE, PP/HTPE (60°C), glassy carbon, Pt	
HClO ₄	70	12	1.67	203 (72.4)	oxidant when hot and concentrated	glass, quartz, PTFE, glassy carbon, Pt, Ta	unless diluted with HNO ₃ prone to explo- sion in the presence of organic matter
CH ₃ COOH	99.5	17.5	1.05	118	none	all	

*The numerals in parentheses represent the acid content (%) in the azeotrope.

Hydrochloric acid readily dissolves most transition metals, metal oxides, hydroxides, carbonates and sulphides, and has strong leaching properties. Chlorides are generally soluble, except for Ag(I), Hg(I), Tl(I) and, to some extent, Pb, Zr and Al. Hydrochloric acid has weak reducing properties so it is often used with oxidants such as Br₂ or ClO₃⁻, H₂O₂ to form nascent chlorine to facilitate the decomposition of more resistant materials. The disadvantages of HCl include its low boiling point (the need for reflux) and volatility losses of some chlorides (As, Sb, Sn, Se, Ge, Hg).

Nitric acid is a strong and good solvent for many metals and alloys and sulphide ores [8]. Nitric acid alone does not dissolve Au and Pt-group metals (except Pd) and passivates Al, Cr, Sb and Sn. Nitrate forms complexes with lanthanides, actinides and Au. The acid can be readily obtained in ultrahigh purity.

Aqua regia, a mixture of conc. HCl and conc. HNO₃ (3+1, v/v), combines the oxidizing power of *in-situ* generated chlorine and nitrosyl chloride with the complexing ability of chloride. It is an almost universal agent for the dissolution of metals and alloys including special steels and noble metals (except compact Ir and Rh).

Perchloric acid is a strong oxidant when hot and concentrated (all the elements except Mn(II) and Pb(II) are pushed to their highest oxidation state) and exhibits a minimal tendency to form complexes. HClO₄ is used for destruction of the organic matter. Perchlorates are readily soluble except those of NH₄⁺, K, Rb, Cs and Ag. Evaporation with HClO₄ converts salts of volatile acids (Cl⁻, NO₃⁻, F⁻) into perchlorates although, when Al or Zr is present, the removal of fluoride is incomplete. Because of the risk of explosion, safety regulations are important, especially in decomposition of mixtures with carbonaceous admixtures.

Sulphuric acid when hot and concentrated chars and destroys completely almost all organic compounds. Because of the formation of insoluble salts with some metals [Pb, alkali earths and, on heating, Cr(III), Al and Fe(III)] H₂SO₄ is seldom used for samples other than organic compounds and refractories. Some elements, e.g. Zr, form complexes facilitating the dissolution. During microwave heating H₂SO₄ is able to dissolve Teflon prior to boiling so its temperature must be monitored. Sulphuric acid converts salts into sulphates on heating. The boiling point and dissolution efficiency are increased by addition of (NH₄)₂SO₄ or NH₄HSO₄.

Hydrofluoric acid is a weak acid, but a strong complexing agent (for Sb, Sn, Zr, Hf, Ti, Nb, Ta and W). It displays no redox properties but

affects equilibria with other oxidants. Many fluorides (e.g. Ca, Mg, Sr, Pb, Al, REE and actinides) are insoluble and when precipitated onto the matrix may produce a shielding effect, thereby reducing the rate of attack with other acids. HF is usually applied to volatilize silicon compounds such as SiF_4 , e.g. in order to liberate trace elements trapped with the silica in biomaterials digests. Fluoride can corrode vessels leading to contamination. To remove fluoride, Al or Be is added. Boric acid is less efficient but it is better suited for analytical practice. In view of the low boiling point of the azeotrope, HF can be purified readily by distillation in Teflon apparatus.

Phosphoric acid forms relatively strong complexes with Fe(III), Mo(VI) and W(VI) and sparingly soluble salts with Zr, Hf, Ti, Sn, Bi, Th and REE even in strongly acidic solution. Because of its low vapour pressure, relatively high temperatures can be obtained even in open vessels. During heating, H_3PO_4 undergoes condensation reactions to produce a mixture of various phosphoric acids [9]. Phosphoric acid has a strong depressive effect in flame techniques. Other acids from the reaction mixture are displaced on heating.

Hydrobromic acid (often with Br_2) is a good solvent for minerals with high contents of As, Sb, Sn, Au, Hg, Ge and Se as well as for iron and cerium oxides. Platinum and some of its alloys resist $\text{HBr}-\text{Br}_2$.

Acetic acid is the most widely used organic acid. It is known to dissolve PbSO_4 and to efficiently leach metal ions out of soils and sediments.

2.1.2 Dissolution techniques

Open vessel dissolution. The boiling point, and thus the attack temperature, can be increased by the addition of an appropriate salt, e.g. NH_4HSO_4 to H_2SO_4 . In most open vessel digestions, refluxing is desired to maintain the volume of acid without the need for continual additions [10]. Open vessel decomposition is prone to contamination and volatilization losses and is seldom used in trace analysis. The decomposition rate can be enhanced by sonication. Samples are then dispersed to form fine suspensions that are readily attacked by acids. The formation of surface films at the interface is suppressed making penetration of the acid into the solid easier. Ultrasonic treatment substantially accelerates leaching of melts by acids and water, as the melt disintegrates rapidly and an increased surface area becomes accessible to the solvent.

Pressure bomb decomposition. A typical decomposition bomb consists of a 20–125 ml Teflon vessel contained in a stainless steel body [11–14].

The pressure build-up inside the vessel increases the boiling point of the acid thereby making the attack faster and more efficient. Low-boiling acids (HCl, HF and HNO₃) can be efficiently used. Lower and easy to control blanks are obtained because less acid is required and airborne contamination is substantially reduced. Furthermore, uncontrolled trace element losses of volatile molecular species are virtually eliminated because of little vapour loss. The disadvantages include a limited sample size (0.1–1 g for organic and 1–5 g for inorganic samples), limited decomposition temperature (200–240°C), and lack of pressure control. Furthermore, as heat transfer through the thick-walled material required to withstand the increased pressure is difficult, heat-up and cool-down times become excessive. Some disadvantages of conventional PTFE bombs can be overcome by using a microprocessor controlled high pressure asher [15] which consists of a quartz digestion vessel in a heated Al-block placed in an autoclave subject to high pressures (14 MPa). Temperatures up to 320°C can be applied. Virtually all organic materials can be decomposed with concentrated HNO₃ only.

Decomposition with acid vapours meets the demanding conditions of determinations of trace impurities in highly pure substances. Vapours employed involve HF, HCl, HBr and HNO₃. The compounds of the analytes contained in the acid should not volatilize. In the ideal case only the matrix reacts and is subsequently vaporized [16].

Microwave-assisted digestion. Microwave heating (usually at a frequency of 2450 MHz) allows much more efficient heat transport than convection because the sample is heated directly [17–24]. Consequently, the decomposition times are considerably reduced (up to 80%) and a smaller excess of reagents is required (lower blanks). The disadvantages of microwave-assisted digestion include the small cavity size and the lack of temperature feedback control. Decomposition in an open vessel has the inconvenience of corrosion of the interior of the oven and the need to cool the oven walls heated by acid vapours. A closed vessel with a safety relief valve placed in the oven cavity is the usual choice. Internal pressures of ca 120 psi can be applied. If more vessels are microwaved at a time they must be rotated during the digestion to ensure uniform exposure of each sample to the microwave radiation. Teflon is an excellent vessel material because of high resistance to acids and a melting point of ca 300°C. Teflon is an extremely poor conductor of heat but very transparent to microwaves, so the solution inside the vessel is heated directly and the vessel walls act as insulators. Quartz is required for concentrated H₃PO₄ and H₂SO₄ which boil above 300°C. Flow-injection systems in

which the sample is digested as it flows through a microwave heating chamber on its way to being analyzed are discussed in Section 7.6. *On-line* and high-pressure closed vessel approaches to microwave-heated sample decomposition have been compared [25].

2.2 FUSION

The fusion process involves a heterogeneous reaction, the rate of which is limited by the contact surface, collection of insoluble precipitate on the surface and diffusion conditions. The high temperatures involved make the fusion attack very efficient. The disadvantages include manipulative difficulties, corrosion of the vessel by fluxes and the resulting contamination, volatilization losses (Hg, Tl, Os, Re, As, Se, Te) and the need for relatively expensive high-purity fluxes and equipment. Platinum crucibles can become alloyed with Fe, Pb, Sn, Sb and Bi and then contaminate other samples. Fluxes partially dissolve the crucible metal. Depending on the reaction involved fusion can be alkaline or acidic, oxidizing or reducing. It is recommended that fusion be avoided where possible and it should never be used (except for XRF) if dissolution can be achieved with acids. The high solid content of the dissolved melt can cause blockages of the nebulizer, burner slot (torch) and sampling orifice (in ICP MS) and results in matrix and spectral interferences. Microwave heating can be applied to fusion [17]. A microwave furnace uses a material with a high dissipation factor, such as SiC, to absorb the total input power in a small area surrounded by a quartz insulation. A temperature of 1000°C in *ca* 2 min can be achieved. The oven is not maintained at the high temperature continuously so less energy is consumed. The user is not exposed to heat when the sample is added or removed.

2.2.1 Alkaline fusion

Alkali carbonate fluxes include anhydrous Li_2CO_3 , Na_2CO_3 and K_2CO_3 , used alone or as the eutectic mixture. The commercial preparations usually lack sufficient purity. Therefore, NaHCO_3 , which is easier to purify and transforms at 300°C into Na_2CO_3 , is often preferred. Oxides, especially Li_2O formed during thermal decomposition of carbonates, lead to the corrosion of Pt crucibles so Zr crucibles should rather be used.

Alkali hydroxides melt at lower temperatures than carbonates but are corrosive for Pt and Pd. Zirconium and glassy carbon crucibles which are resistant should be used.

Alkali peroxides and superoxides are very efficient because of their strong oxidizing properties. Because of their low purity and corrosive nature, they should be avoided except for very resistant materials, e.g. chromites, carbides or nitrides. Potassium superoxide (KO_2) is used where Na^+ needs to be determined [26].

Alkali borates which include metaborates (usually LiBO_2) and tetraborates (borax, $\text{Na}_2\text{B}_4\text{O}_7$) are strong non-oxidizing fluxes. An Li_2CO_3 - H_3BO_3 mixture can be used instead [27]. Metaborate is preferred for acidic rocks whereas tetraborate is more suitable for decomposition of basic materials. The eutectic mixture of LiBO_2 and $\text{Li}_2\text{B}_4\text{O}_7$ (melting point 832°C) is a universal fusion agent for aluminosilicates, oxidic minerals and many ceramics. It is particularly suitable for XRF of light elements owing to low absorption of X-rays. The disadvantages include high viscosity of the melt, introduction of large amounts of boron and wetting Pt by the melt. Crucibles made of Pt-Au and Rh-Pt alloys, which are not wetted by the melt, should be used. Spectroflux[®] and Spectromelt[®] are commercial preparations of alkali borates.

2.2.2 Acidic fusion

Hydrogen sulphates and disulphates are weak oxidants but exhibit strong acidic properties. The former lose water on heating and are converted into disulphates. Above the melting point the melt yields aggressive SO_3 and H_2SO_4 has to be added to reproduce disulphate. Particularly advantageous is NH_4HSO_4 which melts at 147°C and the excess of which can be removed by volatilization at 200°C . Disulphates are mostly used for efficient decomposition of refractory oxides and dioxides. Some binary sulphates K-Cr(III) and K-Al are poorly soluble.

Fluorides display pronounced complexing properties and are efficient agents for decomposition of highly resistant minerals, e.g. zircon or niobotantalates. Insoluble fluorides of Ca, Th and REE are formed. Fluorides are difficult to remove from the reaction mixture.

2.2.3 Reductive fusion (fire assay)

Fire assay involves the fusion of a sample at a high temperature with a flux (Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$), reducing agent (flour, starch), and collector

(usually Pb or NiS). On fusion, a two-phase system, i.e. a slag and the collector button, is formed. The impurities are oxidized and go into the slag while the analytes are collected in the button. The liquid fusion mixture is transferred into an iron mould. When the mass has cooled, the collector button is found beyond the slag in the bottom of the mould. The sample must be fairly fine (150–200 mesh) and representative [28–30]. Fire assay is mostly used in the analysis of minerals, ores and their treatment products for the noble metals. Its major advantage is the applicability to various and large samples (15–50 g) correcting for sampling inhomogeneity. The decomposition is combined with a concentration step as the analytes are extracted from a complex matrix into a relatively simple one which can be analyzed by any instrumental method. Fire assay requires an experienced and skilled assayer to optimize both flux composition and fusion conditions. The equipment is expensive and often bulky. The technique is dirty and large quantities of chemicals are used; blanks need to be run on a regular basis. Samples rich in Cu and Sb form insoluble products in the button. The behaviour of analytes during fire assaying is discussed in detail in Section 11.1.4 and elsewhere in Part III.

Lead fire assay which uses lead produced *in situ* by the reduction of litharge (PbO) as the collector is the most popular. The lead button obtained may have a mass of up to 30 g which is usually reduced by the removal of a large portion of lead and oxidizable impurities by scorification (melting under oxidizing conditions), on a small porous cup (cupel) made of bone or of refractory material. Lead oxide and the non-noble metal oxides are produced and absorbed by the cupel whereupon a silver bead containing quantitatively Au, Pt and Pd and some of the Rh, Ir and Ru remains [28–30].

Nickel-sulphide fire assay makes use of nickel sulphide (NiS) as the collector. On being separated from the slag the button is treated with concentrated HCl to dissolve the NiS. The residue which contains the Pt group elements and some of the gold is filtered off, dissolved in *aqua regia* (or HCl–H₂O₂) and analyzed by a spectrometric technique. The method is favoured over the lead fire assay for the determination of the Pt-group elements in sulphide materials, chromite ores, concentrates and mattes [31–33]. When gold needs to be determined, a separate fire assay collection is recommended.

2.3 DECOMPOSITION IN GAS STREAMS

The sample is attacked with a gas, usually at an elevated temperature. The most popular is combustion of organic materials in air or oxygen but decomposition of oxidic materials in hydrogen or halogens (especial fluorine) is valid for some refractory matrices.

2.3.1 Oxidation (dry ashing)

The technique is based on the oxidation of organic matrix by air or oxygen, usually at elevated temperature. The matrix is thus volatilized as CO_2 and H_2O while the analytes are presumed to be retained in the solid residue. The technique is primarily used for combustion of organic substances (biological materials, coal, peat and petroleum products).

High-temperature ashing consists of heating a test sample in a crucible (usually quartz) which is placed in a muffle furnace. The temperature is slowly raised to *ca* 500°C and then maintained for a few hours. The oxidation is speeded up by enriching the furnace atmosphere with oxygen [34]. Since the mineral residue may be small and light, considerable losses may result from the formation of volatile aerosols. These losses are prevented by adding a mineral collector, e.g. $\text{Mg}(\text{NO}_3)_2$, K_2SO_4 or Na_2CO_3 . Regardless of the precautions taken, dry ashing is prone to losses of volatile elements. At 400°C As, Se and Hg are lost completely, and Ag, Au, Fe, Sb, Zn, and Pb partly [35–38]. The method is slow and prone to contamination.

Low-temperature ashing (oxygen plasma ashing) consists of the combustion of the sample in the radio-frequency excited oxygen or ozone [39]. Excited oxygen (short-lived mono- and diatomic species) formed in a high frequency electric field under reduced pressure is an efficient oxidant at relatively low temperatures (80–200°C). On combustion the oxidation products are cold-trapped. Organic substances alone or present on mineral carriers are readily degraded without the volatilization losses of Sb, As, Co, Cs, Cr, Fe, Pb, Mn, Se and Zn. Losses in Hg, Ag and Au are possible. Low temperature ashing was improved by using plasma excited O_2 and F_2 [40].

Combustion in closed systems involves reacting the sample with oxygen in a sealed container (Schöninger flask) and absorbing the products in a suitable solvent before the flask is opened. Losses of volatile elements can thus be eliminated. In another version the combustion products are trapped in a liquid nitrogen cooled cold finger [34].

Decomposition can be carried out in commercial devices, such as Parr oxygen bombs at a pressure of 2–3 MPa. Most applications of oxygen bombs are concerned with combustion of coal for the determination of Se, As, B, Pb and Hg (*cf.* Section 12.2).

2.3.2 Decomposition with halogens

Nascent *chlorine* supplied by Cl_2 , HCl , S_2Cl_2 , SOCl_2 or CCl_4 or various mixtures which can be obtained in high purity is known to produce highly volatile chlorides of Se, Te, As, Sb, Sn, Si, and Hg. Chlorine attacks nitrides and carbides of many elements including those of B, Cr, Mo, Nb, Ta, Ti, V and Zr. Chlorine has been found to be an excellent reagent for isolation of the REE as well as for the dissolution of Ir and Rh metals [41]. Volatile chlorides such as TiCl_4 and ZrCl_4 are sublimed in trace analysis for these metals.

Fluorine is much more reactive than chlorine and reacts with many elements at only mildly increased temperatures. It requires special apparatus of pure nickel or Monel metal. Oxygen must be removed to prevent the formation of poorly volatile oxyfluorides. The most popular is the decomposition of silicon and boron. Less common examples include formation of volatile fluorides: AsF_5 , GeF_4 , TeF_6 , SeF_6 , WF_6 , MoF_6 , VF_5 , NbF_5 , TaF_5 and TiF_4 when metal oxides are heated (140–400°C in a stream of HF gas) [5]. As a source of fluorine XeF_4 was used.

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Separation and preconcentration

The term *separation* implies the isolation of analyte(s) from the major component (matrix) and/or the separation of the particular analyte from concomitant trace or minor elements. The separation step is an integral part of many analytical procedures because of the need to overcome matrix physical (nebulizer clogging, viscosity), chemical (signal suppression or enhancement) and spectral interferences. *Preconcentration* is an operation in which the relative ratio of trace components *vs* the macrocomponent is increased; it is aimed at overcoming the insufficient detection characteristics of instrumental techniques. The efficiency of preconcentration (enrichment) is defined in terms of recovery (yield): $R = Q_T/Q_T^0$, where Q_T and Q_T^0 are the quantities of the microcomponent in the concentrate and in the sample, and preconcentration coefficient (K) of a desired microcomponent, defined as $K = (Q_T/Q_M)/(Q_T^0/Q_M^0)$ where Q_M^0 and Q_M are the quantities of the matrix before and after preconcentration, respectively [1]. Usually, recovery is calculated as a percentage.

The terms separation and preconcentration often occur together in modern analysis. In practice, the separation/preconcentration step consists either of selectively removing the matrix without affecting the analyte(s) or of isolating the analyte(s) without affecting the matrix. There is a variety of separation/preconcentration methods available [1–14]. The most popular of them include solvent extraction, precipitation, sorption and chromatographic techniques, volatilization and electrodeposition. The choice is dictated by the sample to be analyzed, the analytes (and levels) to be determined and the characteristics of the determination technique. In any case, the incorporation of a separation/preconcentration step increases the analysis time, may result in losses of the analyte(s) and raises demands on the purity of reagents used and the analytical expertise required. This chapter gives a condensed back-

ground to the principles of the most common separation/preconcentration methods indicating their areas of application, advantages and pitfalls. Matrix removal and multielement (group) preconcentration in the analysis of real materials are treated in detail in Part II. Refined and specific methods are discussed elsewhere in Part III.

3.1 SOLVENT EXTRACTION

Solvent extraction is based on the distribution of the analyte or its compounds between two (rarely three) immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water. Stripping (back-extraction) consists of bringing the element from the organic extract back into the aqueous phase. Extraction is universal with respect to the element to be isolated, its concentration and sample type. It can be applied either for the removal of matrix or for the selective (or group) separation of trace elements. Introduction of a combustible extract of trace elements in the flame enhances pulverization conditions and the atomization process [15]. Extraction is usually a fast and simple process which demands only very simple equipment. The disadvantage is a rather low preconcentration coefficient (5–100). Extraction has been the subject of several monographs and topic reviews [16–19]. Preconcentration in multistage extraction was discussed [20].

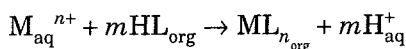
3.1.1 Extractants and extraction solvents

Analyte species which can be readily extracted into the organic phase include uncharged covalent simple molecules (e.g. HgCl_2 , AsCl_3 , BiI_3 , GeCl_4 , OsO_4) or organometallic compounds with a large size-to-charge ratio. In general, metals occur in aqueous solution as hydrated ions which cannot be extracted unless the charge is neutralized. Extraction reagents available for this purpose fall into several basic categories [20–23].

Solvating agents are Lewis bases containing one or more donor atoms (O, N, S) bound to a hydrocarbon skeleton which are able to coordinate to metal cations (Lewis acids). They remove the coordinated water molecules whereas the anion present in the aqueous phase is responsible for the charge compensation. *O*-donor extractants are better suited for example for alkaline earth elements, REE(III), Th, U, Fe(III), Zn,

Mn(II) while *S*-donor reagents are favoured for example for Cu, Ag and noble metals. Solvating extractants include ketones and thioketones, ethers and thioethers, higher alcohols and thioalcohols, alkylphosphates (e.g. TBP) and phosphine oxides (e.g. TOPO). Introduction of anions as metal salts improves extraction efficiency owing to the synergic effect.

Cation exchangers are usually large-molecule organic acids acting according to the equation:



Extraction is favoured by high concentration of the extractant, its lipophilicity and higher pH values. Selectivity which is a function of pH is influenced by the acid dissociation constant. Simple cation-exchangers include fatty carboxylic acids, alkyl-, aryl- and thiophosphoric, phosphonic and phosphinic acids. They are usually viscous liquids, sparingly soluble in water, but easily soluble in non-polar solvents. A popular example is di(2-ethylhexyl)phosphoric acid (HDEHP) [24]. Extraction is usually carried out from strongly acidic solutions into non-polar solvents.

Chelating agents are cation exchangers that have additional complexing properties owing to the presence of a second donor atom in the β -position to the acid functional group. Uncharged chelates are formed when metal ions react with bifunctional (polydentate) ligands such as, e.g., dithizone, 8-hydroxyquinoline, dithiocarbamates, BPHA and acetylacetone. Such chelates are extractable into non-polar solvents provided the ligand satisfies all the coordination sites.

Ion-pairing agents are compounds able to combine *via* electrostatic interactions with oppositely charged analyte ions to form ion associates. The most common are large cations (TPA, TPP, tetraalkylammonium, basic dyes) and high molecular weight tertiary amines (e.g. TBA, TOA). They are usually applied to the extraction of metals readily forming anionic halide complexes, e.g. Cd, Ga, Sb(V), Ir(IV), Pd(II), Au (III), or large anions (e.g. ReO_4^-) into non-polar and polar solvents (see relevant chapters in Part III). A peculiar group is extraction of halometallic acids, e.g. HFeCl_4 , HSbCl_6 , HAuBr_4 or H_2CdI_4 , and heteropolyacids, e.g. Mo(VI), W(VI), Si, P(V), As(V), V(V), Ge, into oxygen-containing solvents. The extraction mechanism involves solvation of the proton(s) by the solvent and often a secondary solvation of the ion pair formed.

Liquid anion exchangers are ion-pairing reagents which include mixtures of higher (7–12 carbon atoms) quaternary alkyl ammonium

salts. They are marketed under trade names, e.g. Aliquat-336, Amberlite LA-1 or Alamine-336.

Macrocyclic compounds (crown ethers) are characterized by the presence of a cavity capable of encapsulating a cation of a defined size [25-28]. Cryptands are macrobicyclic crown ethers. Crown ethers are capable of selective complexation of metal cations with extracting ability depending on the number of oxygen atoms. Simple (non-substituted) crown ethers form cationic complexes that, to be extracted into non-polar solvents, must be associated with suitable anions (picrate, ClO_4^- , BF_4^-). The extraction efficiency of crown ethers can be improved by attaching a proton-ionizable group to the macrocycle host. In a medium basic enough to dissociate off the proton, an intramolecular ion-pair (*zwitterion*) is formed which is hydrophobic enough to be extracted selectively into the organic phase.

Extraction solvents. The preconcentration factor is a function of the difference in solubilities of the extracted compound in water and in the organic phase. The choice of solvent should be also considered in terms of its physical properties, chemical behaviour and compatibility with the determination technique to be used. Density, viscosity and surface tension of the solvent are responsible for the speed of phase separation whereas solubility in water and vapour pressure affect the accurate determination of the concentration factor. The solvent should be chemically inert during the extraction and not interfere during the determination. Solvents for FAAS should have good combustion properties and low viscosity (e.g. MIBK). Halogen-containing solvents should be avoided in GF AAS. High boiling solvents are recommended for ICP techniques to avoid the extinction of the plasma. For NAA and GC-based coupled techniques non-polar volatile solvents are preferred as they can be readily evaporated and separated, respectively, from the analytes.

3.1.2 Separation of traces

The elements readily extractable as complexes with the most important organic and inorganic group reagents are displayed in Fig. 3.1. The practical significance in modern analytical practice is restricted to crown ethers used for alkali, alkaline earths and rare earth elements, the two derivatives of the dithiocarbamic acid, DDTC and APDC, for transition metals and dithizone for metals with high S-affinity. Group preconcentration of traces has the objective of isolating a maximum

[illegible]

Fig. 3.1. Extraction of trace elements with group reagents: O, dithiocarbamates; ●, halides; ■, 8-hydroxyquinoline; ★, β -diketones, ▲, crown ethers.

number of elements in a single step using a minimum number of reagents the excess of which should be retained in the aqueous phase. On the other hand, by the choice of appropriate pH and sometimes using appropriate masking agents these reagents may become highly selective and even specific. In some cases exchange techniques may prove very useful, in which a less stable metal chelate is the source of the chelating agent.

3.1.3 Separation of the matrix

Extraction is an efficient technique for the removal of matrix provided that the capacity of the organic phase is large, the extraction is sufficiently selective for trace elements to remain in the aqueous phase and the analyzed sample has a relatively simple macroelement composition. Metal chelates (with exception of cupferronates and acetylacetonates) are generally not suitable because of their moderate solubility in organic solvents. Matrix extraction systems are shown in Fig. 3.2. The most popular systems include halides, nitrates and carboxylic acids.

3.1.4 Practical aspects

In the majority of cases extraction is a batch process carried out in a separatory funnel. In ultratrace analyses tapered or specially profiled quartz tubes are rather recommended because of easier cleaning (more compact size), less contaminating material, and easier centrifugation in case of difficulties with the phase separation. Shaking must be continued until equilibrium is reached, which may last seconds, minutes or (rarely) hours depending on the system; more than 2–5 min requires a mechanical shaker. If no large preconcentration factors are required, microscale extraction carried out in autosampler tubes followed by direct automatic introduction of the organic phase into the atomizer is recommended.

Continuous-flow extraction involves segmenting of an aqueous stream with an organic solvent and separation of the phases using a membrane separator [29–31] (*cf.* Section 7.2). It is seldom used in practice because the preconcentration factors are small and solvent consumption is large. An interesting possibility is offered by the counter-current extraction in which the organic phase is retained by gravitational forces whereas the aqueous phase is pumped through it [32].

[illegible]

Fig. 3.2. Matrix extraction systems in analytical chemistry: O, oxides; ●, halogenides and oxyhalogenides (also on saturation with HCl); ■, as sulphates; ☒, as nitrates; ◇, as organic compounds.

3.2 PRECIPITATION AND COPRECIPITATION

Separation by precipitation is based on the differences in solubility of the compounds formed by the analyte and by the concomitant elements (matrix) in aqueous (less commonly aqueous-organic) solution. Precipitation methods are used either for selective separation/preconcentration of traces or for matrix removal leaving the analyte(s) in the supernatant solution. The particular process by which dispersed solid or liquid particles present in an aqueous solution are transported to the solution surface with the aid of a rising stream of gas bubbles or non-polar solvent droplets is called flotation. The substance to be floated should be hydrophobic or converted to a hydrophobic substance by means of surfactants.

3.2.1 Coprecipitation of traces

To reach the quantitative precipitation of a trace analyte the presence of a collector (scavenger, carrier) is required and the process is called coprecipitation. Apart from ensuring selective and quantitative precipitation, a collector should be easy to separate from the solution and should not interfere with the subsequent determination. The carrier may already be present in the analyzed sample or be added. In contrast to extraction, coprecipitation is not restricted by the very low concentration of the trace species. The most important coprecipitated forms of particular elements are summarized in Fig. 3.3 whereas an exhaustive list can be found elsewhere [33]. The most widely used is coprecipitation with hydroxides, reductive precipitation and precipitation with organic carriers.

Hydrous oxides (hydroxides) usually include $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{La}(\text{OH})_3$, $\text{Zr}(\text{OH})_4$ and MnO_2aq . They are particularly suitable for group concentrations from very dilute solutions of salt-rich matrices but suffer from fairly poor selectivity. $\text{Fe}(\text{OH})_3$ is the most popular as it is usually already present in the sample. $\text{La}(\text{OH})_3$ is recommended for AAS and spectrophotometry while $\text{Al}(\text{OH})_3$ gives a fairly simple matrix for ICP AES. Amphoteric metals such as Al, Pb, Cr, Sn and Zn remain unprecipitated with NaOH while when NH_3aq is used metals forming ammino complexes (e.g. Ag, Cu, Ni, Co, Zn, and Cd) remain in solution. Easily hydrolysable species [e.g. $\text{Sn}(\text{IV})$, $\text{Sb}(\text{V})$, $\text{Tl}(\text{III})$, $\text{Bi}(\text{III})$] are separated from acid medium with MnO_2aq (formed by reacting Mn^{2+} with MnO_4^-) as the collector. Elements coprecipitated as hydroxides can

[illegible]

Fig. 3.3. Coprecipitation of trace elements in analytical chemistry: O, hydroxides or acids; □, sulphates; ■, phosphates; ☒, fluorides; ∅, oxalates; ▲, elements; ☆, 8-hydroxyquinolates.

be isolated by organic reagents of the R.OH type, such as 8-hydroxyquinoline, cupferron or β -diketones.

Reductive precipitation. Elemental carriers (e.g. Se, Te, Hg) are obtained by reduction *in situ* using NH_2OH or NaBH_4 . It is particularly useful for ultratrace preconcentration of electropositive metals and exclusion of major and minor matrix elements such as Ca, Mg, K, and Na and analytical interferences associated with them.

Organic collectors are particularly suitable for GF AAS as they can be easily removed by *in-situ* ignition of the precipitate (graphite furnace) giving rise to very sensitive methodologies. Activated charcoal, cellulose and chitin can serve as a collector in isolation of many trace elements precipitated in various forms [34,35]. Charcoal is often used for the preconcentration prior to INAA since it is not activated.

Flotation. Theory and applications of foam flotation have been reviewed [36]. In precipitate flotation trace ions are quantitatively coprecipitated with a small amount of collector which is then floated [37]. In ion flotation, traces of, usually complex, ions, are floated with the aid of surfactant ions of opposite charge. In solvent flotation, the analyte is chelated to form a multivalent anionic complex able to associate with large-size organic cations (e.g. basic dyes). The ion associates can form adducts with simple dye salts which are hydrophobic and accumulate at the phase boundary or on the wall of the separating funnel during shaking with a non-polar solvent [38].

3.2.2 Precipitation of macrocomponents

The precipitation of macrocomponents to separate them from trace elements is less common but nevertheless some efficient methods exist. The major concern is to prevent the bulky precipitate from entrapping the determined traces whereas the quantitateness of the precipitation is less important [39].

Precipitation methods with a minimum addition of easily purifiable reagents (acids, NH_3aq) or with no addition at all (electrolysis) are favoured. Preconcentration methods are subject to losses of analytes owing to their adsorption on the precipitate, mixed crystal formation and post-precipitation effects. The verification of the yield should be checked by isotope tracer recovery studies. The losses can be minimized by choosing a precipitate with a minimum specific surface, complexation of supernatant analytes and not insisting on the quantitative removal of the macrocomponent. Most commonly the macrocomponent

is precipitated in the elemental form on reduction (electrolytic or chemical) (e.g. Au, Ag, Hg, Pt-group metals, Se, Te) or as a hydrated chloride (e.g. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$) [39].

3.3 VOLATILIZATION

Methods of this class are based on differences in the vapour pressures of individual elements or their compounds. The physical separation is usually preceded by chemical conversion of trace analytes (or matrix) to a volatilizable species; only simple covalent compounds are sufficiently volatile to be distilled, sublimed or evaporated. Methods based on selective volatilization include: (1) purging of trace elements (or their compounds) from the matrix, (2) evaporation of the matrix, either direct or on a chemical conversion, and (3) separation of trace element compounds from each other (gas chromatography) (see Section 3.5.1). The relevant elements and their volatile species are summarized in Fig. 3.4.

3.3.1 Volatilization of trace elements

Volatilization techniques based on the formation of element vapours, hydrides, halides, oxides and sometimes organic compounds have been reviewed [40]. The volatile species formed are purged from the solution by an inert gas (H_2 , N_2 or Ar) which usually also acts as a carrier transporting the species to the detector. Volatilization can be carried out in batch mode (usually with cryofocusing), continuous-flow mode and flow-injection mode.

Mercury is the only metal to be readily purged from an aqueous solution (cold vapour generation). Mercury(II) is reduced in solution and the Hg^0 formed is purged and transported directly to the atomizer or focused on gold gauze which is then heated (*cf.* Chapter 36).

Hydride generation has been the subject of several reviews [41–46]. Volatile hydrides are formed by elements of groups IVA (Ge, Sn, Pb), VA (As, Sb, Bi) and VIA (Se and Te) and their alkyl derivatives [47] on their reduction in an acidic solution. The NaBH_4 –HCl system is superior to other reductants in terms of the reduction yield, reaction time, blank value and versatility. The hydride formed is swept out of the generation vessel with an inert gas and carried into an atomizer or excitation source, directly or on cryofocusing. Optimum reaction conditions are strongly element and species dependent so perspectives for

simultaneous multielement analysis are rather poor. Hydride generation is extremely prone to interferences, especially with transition metals which either compete for the NaBH_4 (and thus reduce the rate and yield of hydride formation) or form precipitates which adsorb the generated hydrides or catalyse their decomposition [41–48]. Interferences are alleviated by various masking agents (EDTA, thiourea, and ascorbic acid) but an additional separation step (coprecipitation, solvent extraction or sorption) seems to be inevitable for complex samples. Accuracy of the results is severely affected by small variations of the speciation of the analyte in the sample, reaction variables and the quality of the reagent used, so a full quality assurance system should be instituted in a laboratory.

Ethylation with sodium tetraethylborate (NaBEt_4) is an efficient method of generating volatile compounds of Pb, Sn, Hg, Se, As and their alkyl and aryl derivatives [49,50]. The method is less interference prone than hydride generation.

Other systems. β -Diketones (acetylacetone and trifluoroacetylacetone) [51] and dithiocarbamates [52,53] form chelates with some metals (e.g. Cr, Cu, Fe, Zn, Co, Mn) which can be volatilized at temperatures above 100°C [51]. Osmium, Ru and Re can be volatilized as oxides (*cf.* Chapters 40, 44 and 47) and Ni as the carbonyl (*cf.* Chapter 38). Slow formation of carbonyls of Fe and Co has been observed [54]. High temperature volatilization of chlorides (Bi, Cd, Ge, Mo, Pb, Sn, Tl and Zn) and fluorides (Mo, W, U, V, Re and Ge) has been discussed [52].

3.3.2 Volatilization of macrocomponents

Evaporation of the matrix is an efficient method of concentration of traces, unless they are volatile as well. The matrix can be removed intact (distillation) or converted by means of a chemical reaction to a volatile species. Methods for the volatilization of macrocomponents were reviewed in an old but still important paper [55].

A classic approach is the evaporation of water, an organic solvent, a volatile acid or NH_3 solution. Infrared surface heating and clean air cabinets are recommended to minimize losses and contamination, respectively. Graphite furnace AAS achieves internal preconcentration by *in-situ* evaporation in the drying step. The addition of “keepers” is a must. When volatile acids are evaporated H_2SO_4 is added to fuming. Trace elements behave in a different way and may be lost (e.g. Hg, Se, B) unless complexed to a non-volatile compound (e.g. boron with man-

nitro, *cf.* Chapter 19), especially if present as organically bound covalent compounds. Distillation of the matrix is also a way to remove chlorine, bromine, iodine, sulphur and mercury.

3.4 SORPTION

Sorption is a convenient and rapid method of preconcentration capable of attaining high concentration factors. The mechanism of sorption can be either physical or chemical. The efficiency of sorption is usually described by the distribution coefficient which is defined by the ratio of the total amount of an element in a unit quantity of the sorbent to the total amount of the element in a unit quantity of the solution. More often, however, the performance of a preconcentration method is assessed by measuring the percentage recovery. Another parameter (in a column mode) is the measurement of the total volume which can be passed through the column without losses to occur, which is defined as the breakthrough volume of the column. The selectivity is given by the ratio of the distribution coefficients of two elements of interest and is expressed as the selectivity coefficient. Preconcentration by sorption has been the subject of several reviews [56,57].

3.4.1 Sorption *via* physical interactions

Charcoal (activated carbon) is a common sorbent for trace organic compounds because of a very large hydrophobic surface per mass unit. Charcoal is able to adsorb mercury and gold from dilute HCl solutions (*cf.* Chapters 28 and 36), most transition metals in a slightly alkaline medium and virtually all elements provided that they are complexed, e.g. with dithiocarbamate, 8-quinolinol or other reagents [58].

Silica, especially C₁₈-bonded (octadecylsilica) available in cartridges, membranes (extraction disks) or microcolumns, is used for the preconcentration of metal complexes (8-hydroxyquinoline, dithiocarbamates) formed beforehand in the aqueous phase [59–61]. The complex is usually eluted with methanol.

Macroporous polymers show relatively low resistance to flow and are not vulnerable to solvent change in terms of shrinking. The best known of them include styrene-divinylbenzene copolymers, Amberlite XAD-1, -2 and -4, and methyl methacrylate based polymers, Amberlite XAD-7 and -8 resins. They are effective sorbents for organically bound trace

metals (e.g. iron complexes with humic and fulvic acid) or metal complexes [99]. Some of them (e.g. SM-7 and XAD-7) were found to preconcentrate free metal ions directly from aqueous solution *via* ion-exchange on impurity sites [62].

Plastic foams are defined as plastics on which an open structure has been conferred by inclusion of gas to form numerous small cells. There are both rigid and flexible foams, with open or closed cells. Polyurethane foams are the most widely popular. Unloaded polyurethane foams can be selective sorbents for trace metals provided that the composition of the aqueous solution is suitable. The properties and analytical characteristics of plastic foams have been reviewed [63–67].

Algae were reported to be efficient sorbents for many metals [68,69].

3.4.2 Simple ion exchange

A solid ion exchanger is an insoluble framework to which ionic groups are attached and which contains mobile cations (cation exchangers) or anions (anion exchangers). The ion exchangers are either (1) large surface area inorganic materials with fixed ions and an electrical double layer or, (2) porous (on the molecular scale) organic resins. The theory and applications of ion exchange have been reviewed [70].

Inorganic ion exchangers include (1) poorly crystalline or amorphous materials such as hydrous oxides of Sb, Si, Sn, Ti, Th, Zr and Al, and (2) crystalline materials such as aluminosilicates (zeolites), clays and insoluble ammonium and alkali metals ferrocyanides or salts of heteropoly acids (e.g. molybdo- or tungstosilicate, -phosphate and -arsenate). These ion exchangers enjoy fairly large stability at a high temperature and in the presence of ionizing radiation but suffer from low capacities and poor chemical and mechanical properties. The most popular use is for radiochemical separations in NAA, especially that of $\text{Sb}_2\text{O}_5\text{aq}$ for the removal of Na^+ [71].

Synthetic ion-exchange resins are usually styrene–divinylbenzene copolymers in the form of spherical beads treated to introduce ionizable functional groups. The functional groups in cation exchangers are $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ while these in anion exchangers are $-\text{NR}_3^+$, $-\text{NR}_2$, $-\text{NHR}$ and $-\text{NH}_2$. The most popular are strong cation exchangers with $-\text{SO}_3\text{H}$ groups (Dowex) and strong anion exchangers (Amberlites) with $-\text{NH}_3\text{OH}$ or $-\text{NH}_3\text{Cl}$ groups.

Natural polymers such as cellulose modified to form a dibasic phosphate ester (Cellex P) or triethylamino group (Cellex T) [72] have been

used. Preparation of chemically modified cellulose exchangers and their use for the preconcentration of metals have been reviewed [73].

3.4.3 Chelating sorbents

The ability of chelating agents to bind metal ions makes them effective sorbents. Resins can be impregnated (by physical adsorption) with a chelating agent or chemically modified by the introduction of functional groups.

Reagent loaded sorbents. Loading with a reagent is a convenient and versatile method of improving the selectivity and efficiency of bare sorbents. A variety of impregnating reagents including *S*-donor compounds, azocompounds, oximes and liquid extractants (LIX type, Kelex 100, Alamine 336) have been proposed [70]. The common supports include the XAD resins, foams, silica or controlled pore-size glass beads (CPG). Foams with large available surface area are particularly suitable for the immobilization of considerable amounts of a chelating agent, often as a solution in an organic solvent, thus improving the process kinetics. Silica gel or CPG beads are excellent support materials owing to their porosity, large surface, resistance to acids, heat, swelling and mechanical strength. Practical applications of reagent loaded resins are hampered by the gradual washing out of the loading by the eluent and decreasing column efficiency. Sorption on polymer-based supports and renewable reagents has been discussed [74].

Sorbents with immobilized functional groups include natural polymers (cellulose, chitin and a product of its deacetylation, chitosan), synthetic polymers or silica gel (glass) which have been chemically modified to introduce a chelating group. Several sorbents functionalized with chelating groups are commercially available as filtering disks [75]. The silanization of the silica surface to render it hydrophobic is essential prior to introduction of functional groups which makes the preparation of ligand-immobilized silica complicated and time-consuming. 8-Hydroxyquinoline is the most popular ligand [76,77]. Synthetic polymers (e.g. cross-linked styrene-divinylbenzene) can be chemically modified to contain oxygen groups (hydroxyl, phenolic, carboxylic, carbonyl, ether or phosphoryl), nitrogen (amine, amide, azo, nitro, nitroso or nitril group) and sulphur (thiocarbamate, thiol, thioether or disulphide group) to produce a variety of resins [56]. The most popular are resins with an iminodiacetate functional group, e.g. Chelex-100 [56,78], dithiocarbamate (poly-DTC) [56,79] and dithizone [80]. The Chelex-100 resin suffers from the large

changes in volume with change in ionic form which significantly alters flow rate. The second problem is that the optimum pH range 5-5.8 covers the range where many metals hydrolyse and precipitate, especially Fe(III) and Cu(II). The retained analytes can be eluted, and the resin can be ashed or introduced into the plasma *via* ETV. The use of chelating resins has been the subject of comparisons [81] and reviews [82,83].

3.4.4 Practical aspects

Sorption can be performed in a batch or column mode. In the former, a sorbent powder is added to the sample and the mixture is then stirred (or shaken) for some time whereupon the sorbent is filtered off. In the column mode, a sorbent is packed into a suitable column through which a sample solution is passed. The advantages of the column mode include a higher sorption efficiency, ease of adaptation to different volumes of sample available and easy cleaning and automation. The dimensions and nature of the column depends on the application and a lot of preconcentration cartridges are commercially available. Column preconcentration can be performed *off line* or *on line*. In the *off-line* mode the support with the sorbed analyte is usually ashed. The *on-line* preconcentration, in which the sorbent column is coupled directly to the analytical instrument, will be discussed in more detail in Section 7.4.

3.5 CHROMATOGRAPHIC TECHNIQUES

Chromatographic methods are based on dynamic partitioning of analytes, carried by a mobile phase through a stationary phase, between these two phases. The fraction of time a solute spends in each phase is determined by its distribution coefficient, which must be different from those of the other solutes for a separation to occur. Packed columns contain a stationary phase of small solid particles (often coated with a thin layer of liquid) in an open tube. In the case of open tubular or capillary columns a liquid is forced through a small-diameter tube. A thin layer of the liquid coats the inside wall of the tube and is held there by capillary forces or by chemical bonding to the tube surface. Chromatographic techniques are usually divided according to the nature of the mobile phase into gas, supercritical fluid and liquid chromatography. Chromatographic techniques in inorganic analysis have been reviewed [84–87].

3.5.1 Gas chromatography

In GC an analyte in gaseous phase is partitioned into a stationary liquid phase. The involatility of metals under normal ($<400^{\circ}\text{C}$) conditions and the lack of a readily applicable derivatization procedure to render them volatile and thermally stable restrict the practical role of GC to speciation analysis for organometallic compounds [88,89].

Derivatization in GC. Native forms of some organometallic compounds occurring in real materials are volatile enough to be gas chromatographed. They include tetraalkyllead species ($\text{Me}_n\text{Et}_{4-n}\text{Pb}$), methylselenium compounds (e.g. Me_2Se , Me_2Se_2), some organomercury compounds (MeHg^+ , Me_2Hg) and geoporphyrins. The majority of inorganic and organometallic species have relatively high boiling points and/or poor thermal stability. To be amenable to GC they must be converted to non-polar, volatile and thermally stable species. The derivative chosen must retain the structure of the element-carbon bonds, if present, to ensure that the integrity of the species remains unaltered. The most common derivatization methods include: (1) conversion of small inorganic and organometallic ions into volatile covalent compounds (hydrides, ethylated species) in aqueous media; (2) conversion of larger alkylmetal cations: e.g. $\text{R}_n\text{Pb}^{(4-n)+}$ with Grignard reagents to saturated non-polar species and (3) conversion of ionic species to fairly volatile chelates (dithiocarbamate, trifluoroacetone) or other compounds. Frequently the volatile derivatives are concentrated by cryotrapping or extraction into an organic solvent prior to injection into the gas chromatograph.

Thermal desorption. In the earliest and simplest instrumental configuration the U-tube used as a cryotrap for highly volatile organometallic species, either native, e.g. air gaseous phase, or on derivatization, e.g. by hydride generation or ethylation (*cf.* Section 3.3.1) is immersed into a hot water bath which stimulates the release of the species retained discriminating them according to the boiling point [47]. The set-up is simple and cheap. The resolution is poor but sufficient for most environmental applications. The restriction is that the analytes must be fed as moisture-free gases.

Packed column GC can be considered as an advanced form of thermal desorption chromatography. The ability to accept analytes injected as solutions (10–50 μl), usually in non-polar solvents, extends the range of applications beyond compounds derivatized using Grignard reagents. Non-polar phases have been recommended in the literature for the

separation of organometallic species [90]. Packed columns, usually filled with Chromosorb W containing a 3–10% loading of OV-101 or Carbowax, are the most widely used in speciation studies. The oven programming improves considerably the separation compared with thermal desorption. The peaks are broad and some compounds may not be resolved, especially in the case of close molecular masses (volatilities) of particular compounds and/or their different concentrations.

Open-tubular GC makes use of megabore or capillary columns with polymethoxysilane coatings (DB-1, HP-1, RSL-150) which provide higher resolution and sharper, more concentrated bands. The high resolution of capillary columns is essential for the analysis of complex environmental and especially biological samples. The inert nature of capillary columns makes them superior for the separation of organometallic species containing very polar bonds (metal–halogen) which may strongly interact with the packed column often resulting in the decomposition of the analyte and peak tailing. Other advantageous features of capillary columns include flexibility, ease of use and diversity of coatings available. The restricted capacity of capillary columns is overcome by using retention gaps, electronic pressure control or solvent venting techniques [89].

3.5.2 Liquid chromatography

Liquid chromatography is based on the interaction of analyte in the mobile phase with a solid or liquid stationary phase by a variety of mechanisms including adsorption, partition, ion exchange or size exclusion. The early gravity fed LC systems with fairly large-size (100–200 μm) packings have been replaced by 5–10 μm packings which are more easily incorporated in *on-line* systems and are fed by peristaltic or high pressure pumps (high performance liquid chromatography, HPLC). The most common packings in HPLC include silica: bare, chemically bonded or coated as exemplified in Table 3.1. Liquid chromatography in inorganic analysis has been reviewed [91–94].

Partition chromatography is based on a bulk-phase distribution process in which the solute forms homogeneous solutions in each phase. In the normal-phase mode highly polar stationary phases (usually chemically bonded with amino or cyano groups) and relatively non-polar mobile phase are used. The least polar solute is the first to be eluted whereas retention times decrease with increasing polarity of the mobile phase. In the reversed-phase mode the mobile phase is polar whereas

TABLE 3.1

Stationary phases in HPLC

Support	Adsorption	Partition		Ion exchange	
		Normal	Reversed-phase	Cation	Anion
Macrosphere®			C ₄ ,C ₈ ,C ₁₈	WCX,SCX	WAX,SAX
Nucleosil®	Silica	CN ⁻ ,diol	C ₈ ,C ₁₈ ,phenyl	SA	SB
Spherisorb®	Silica	CN ⁻ ,amino	ODS-1,ODS-2	SCX	SAX
Partisil®	Silica	PAC	ODS-3,C8	SCX	SAX

the stationary phase is non-polar (usually C₁₈-bonded silica). Polar substances prefer the mobile phase and are eluted first followed by the nonpolar solutes. In modern methods the molecules constituting the stationary phase are covalently bonded to a silica or silica-based support particle. The mobile phase is aqueous but contains polar organic solvents in various proportions to overcome the insufficient stability of analyte complexes in water. An addition of complexing agents (dithiocarbamates, 8-hydroxyquinoline, PAR, PAN, dialkyldithiophosphates and hydrazones) to the polar phase is used to improve the separation.

Ion-interaction chromatography (IIC) is based on the distribution of an ion pair (analyte-counterion) between a non-polar stationary phase and a polar mobile phase. The same columns and mobile phases are used as in reversed phase LC. The mobile phase includes anion pairing reagent, acid-base buffer, complexing agent (EDTA, tartrate) and sometimes an organic solvent. The technique is often called ion pair chromatography or, if the ion pairing reagent is an active surfactant (detergent), micellar liquid chromatography. Micellar chromatography is advantageous because organic mobile phases can thus be avoided which increases the sensitivity of plasma detection. Two operation modes are possible. The first involves column conditioning with the ion pairing agent which is adsorbed on the mobile/stationary phase interface and thus omitted then from the mobile phase. The other mode involves addition of the ion pairing agent to the mobile phase and thus dynamic coating of the stationary phase. Both cationic and anionic species can be separated by IIC. As counterions large anions (butane-, pentane- or dodecylsulphonate) or cations (TBA, heptyltriethylam-

monium) are used. In some cases a chelating agent (EDTA) or other complexant (F^-) is used to form a negatively charged complex of the analyte species which is ion paired with a suitable large-size cation.

Ion exchange chromatography (IEC) is based on the reversible exchange of ions between the solid ion exchange resin and a liquid eluent. Both pellicular and porous microparticles have been adapted for use with ion exchange chromatography by coating the rigid silica particles with a thin layer of a non-porous ion exchange resin. The capacity is 100-fold less than for the resins used in batch separations but separation is considerably improved making the technique able to resolve even very similar species of the same element. The simplest IEC of metal species is based on affinity differences of the native analytes for the column. Separation is controlled by pH and ionic strength of the eluent which competes with sample species for ion exchange sites and elutes the sample from the column (push mechanism). The efficiency of separation can be increased by adding to the eluent a complexing reagent which changes the form of the sample species allowing it to move down the column more easily (weaker retention, pull mechanism). Eluents in IEC are aqueous solutions, containing 0.05–0.3 M ionic solute in the mobile phase. Proton (supplied by acids) is a favourite eluting agent for the separation of cations because its binding capability can be adjusted easily through the use of pH buffers. Small fractions of water-miscible polar solvents (lower alcohols) are sometimes added to increase the solubility of analytes, e.g. tributyltin (TBT). An ion-exchange resin will bind all ions of the opposite charge type. The range of applications of IEC can be expanded by converting metal cations to anions through complexation with a negatively charged ligand which also makes the technique applicable to simultaneous separation of cations and anions.

Size-exclusion (or gel-permeation) chromatography (SEC) is based on the molecular sieve effect and enables the separation of substances according to their size and to a lesser extent, shape. The stationary phase material is characterized by a network of uniformly sized pores in which certain molecules can diffuse. The average time a substance spends in the pores is determined by its size which for a given shape, can usually be related directly to its molecular weight. Albeit few studies on small molecules (porphyrins, humic and fulvic acids) have been carried out, the principal use of SEC in analytical chemistry of metals is the separation of metallothioneins (*cf.* Chapters 20 and 65).

3.5.3 Supercritical fluid chromatography

The mobile phase is a supercritical fluid, i.e. a fluid at pressures and temperatures above its critical point, whose physical properties are intermediate between those of gases and those of liquids. Carbon dioxide (sometimes doped with a modifier such as methanol or SF_6) is the most commonly employed mobile phase. The efficiency of SFC is comparable with that of GC because the mobile phase has low viscosity and high solute diffusivities. On the other hand, the solvating power of the mobile phase which can be controlled by the temperature and pressure can approach the HPLC values with the molecular weight limit of up to *ca* 7000 daltons. Consequently, thermally labile, non-volatile and high molecular weight compounds which are not easily gas chromatographable can be separated with shorter analysis time and lower solvent consumption than required for LC. SFC in hyphenated techniques was recently reviewed [95]. Supercritical fluid chromatography offers the ability to separate native organometallic species (without derivatization) with gas phase sample introduction and thus high sensitivity.

3.6 ELECTROCHEMICAL METHODS

This class includes methods based on the electrochemical reduction (more seldom oxidation) of the ions present in the solution followed by the accumulation of the redox product on (or in) the cathode (element or an intermetallic compound, e.g. amalgams) or anode (e.g. MnO_2 , PbO_2) [96]. The behaviour of an element during electrolysis is governed by the Nernstian equation and depends on the element itself, its chemical form, concentration and electrolyte composition (ionic strength) but also material (overpotential) of the electrode and the design of the electrochemical cell (mixing). Separation is based on electrode potential control; the analytes are simultaneously concentrated onto a small electrode area from a highly dilute solution. Electrolytic separation/preconcentration methods for spectrometric analysis are divided according to how the deposit is transferred to the atomizer into those based on oxidative redissolution into a smaller volume of solution and those followed by thermal vaporization.

Anodic stripping voltammetry (ASV) is based on the reversible deposition of metal ions on a mercury film or mercury drop electrode, or a bare glassy carbon or gold electrode and then oxidative stripping by an

anodic voltage scan [97,98]. The main disadvantage is the practical limited application to amalgam forming metals (Cu, Pb, Cd, Zn, Sb, Bi, In, Tl and Ga). The ASV methods were applied to AES [99] and MS [100,101]. Usually, preconcentration is done in the batch mode but ASV flow cells have also been described [101].

Electrolytic preconcentration with electrodes including the mercury drop [102] and film [103], refractory wire and loops, graphite rods, tubes and cups [104–106] and glassy carbon slides [107,108], usually with controlled potential deposition, has been described. Electrodeposition on mercury electrode is more versatile owing to the low overpotential for reduction of proton with graphite electrodes only a few metals can be deposited directly onto the carbon. Following the deposition mercury may then be easily vaporized and filaments can be heated with an electric current while graphite cups are directly inserted into the atomizer. The slides can be directly analyzed by XRF.

Electrochemical methods require that the interfering matrix components be electrochemically inactive (NaCl , AlCl_3) whereas the trace component(s) to be electrodeposited must be present as labile and active species. Metals complexed or adsorbed on colloidal species may not be deposited unless released by, for example, UV irradiation or acid digestion. This disadvantage may turn into an advantage when information on speciation of the metal is sought [109]. Electrochemical methods lack the versatility for multielement preconcentration and are time consuming but their advantages in terms of sample size required, concentration factor, simplicity and freedom of contamination make them of interest for customized applications especially in ultratrace analysis. Electrodeposition of the matrix is less convenient and is seldom suitable for multicomponent materials (alloys). For high purity metals, however, the matrix can be dissolved by anodic oxidation and redeposited on the cathode while less electronegative traces remain in solution [110].

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Spectrometric determination techniques

Several general monographs on principles and instrumentation in spectrometric analysis appeared [1–10]. Extensive progress reports on particular instrumental techniques appear biannually in *Analytical Chemistry* (R pages) and in *Journal of Analytical Atomic Spectrometry*. Trends in analytical chemistry have recently been evaluated [11].

4.1 BASIC CONCEPTS

Sensitivity is usually defined as the slope dx_a/dc of the calibration curve of net analyte signal (x_a) vs concentration (c) and is expressed in terms of the signal intensity per unit concentration of an analyte. In AAS the sensitivity is often identified with the characteristic concentration (m_0) defined as the concentration of an element needed to produce a signal of 0.0044 absorbance unit (equivalent to a 1% decrease in the transmitted radiation). The sensitivity is not a determinand of the minimum detectable amount of the element which is also affected by the background noise.

Detection limit (DL) is defined by IUPAC as an amount of analyte producing a signal (corrected for blank) x_a equal to three times the standard deviation of the background signal σ_B , considering a normal distribution and 99.87% confidence level. If $x_a < 3\sigma_B$, the element cannot be detected; if x_a is between $3\sigma_B$ and $10\sigma_B$ only qualitative detection is possible, and if $x_a > 10\sigma_B$, quantitative determination of the element is possible. The background signal is measured at the analytical wavelength (mass) for a blank solution. The standard deviation is estimated from 11 consecutive integrations, or is defined as $2.3 \sqrt{N}$ where N denotes the total number of detector counts in the background area [12].

The response can be expressed in counts per time unit or in total counts (i.e. multiplied by the integration time). The values obtained in these two ways can differ. Background is influenced by the sample matrix (e.g. Compton continuum, non-specific molecular absorption or emission, other analyte line overlap) so the estimates from the blank lead to unrealistically low values. Measurement of the background signal in the sample on either side of the analyte line is more reliable as the effect of sample matrix is taken into account. As the final quantification in any analysis is the result of blank subtraction, either explicit or implicit, to produce the net spectral intensity the variance is doubled, increasing the DL by a factor of $\sqrt{2}$. Errors in sample handling prior to instrumental determination also introduce additional variance into the total error. When DLs are compared it must be borne in mind that some methods, e.g. LA ICP MS offer extremely low ADLs but because the amount of the actually analyzed sample is small, high relative DLs are obtained. The concept and definitions of the DL have been extensively discussed [12–16].

Precision refers to the agreement between values in a set of data. According to IUPAC precision represents the random uncertainty in the value for the measure, x_a , or the corresponding uncertainty in the estimate of concentration, c . This is expressed in terms of standard deviation (SD) or relative standard deviation σ_a

$$\text{SD} = \left[\frac{\sum (x_{a_i} - \bar{x}_a)^2}{N - 1} \right]^{1/2}, \quad \sigma_a = \frac{\text{SD}}{x_a}$$

Two levels of precision are recognized: *repeatability* which is the random error associated with a single test operator and instrument under constant operating conditions on identical test material, and *reproducibility* defined as the random error associated with different test operators and different instrumentations analyzing the same test material [17].

Accuracy relates to the agreement between the measured concentration and the “true value”. The limitations of accuracy in terms of random and systematic errors are discussed in Chapter 8.

Dynamic range refers to the concentration interval over which a calibration curve is linear. The dynamic range starts at the DL and ends when the curve starts to bend. A large dynamic range permits simultaneous multielement analysis using the most sensitive line for each element from one dilution. Analytical range is defined as the concentration

interval within which a predefined value of % in the concentration is not exceeded [18].

Selectivity is defined in terms of the ratio of signal intensities produced by an analyte and interferent(s) at the analytical wavelength. In MS techniques selectivity is usually considered in terms of abundance sensitivity which is a measure of the ability to detect an ion at a mass-to-charge ratio adjacent to that of an ion present at a high concentration. It is defined as the ratio of the intensity of the tail of the major peak (at the mass of the minor isotope) relative to the intensity of the major peak itself.

4.2 SAMPLE AND SAMPLE INTRODUCTION

For the measurement a test sample must be reproducibly and efficiently transferred to the optical cell (atomizer, excitation source). The sample introduction system determines the sample amount required, sample throughput, experimental sensitivity (transport efficiency), precision and, to a large degree, interferences. The variety of materials to be analyzed falls in four major categories, gases, liquids, slurries and solids, each of which requires a customized approach. Sample introduction in atomic spectroscopy has been extensively discussed [19–23].

4.2.1 Gaseous samples

Gaseous samples are favoured in atomic spectroscopy because of high transport efficiency, no energy loss for desolvation and general freedom of matrix interferences (usually separated during the volatilization step). Mercury cold vapour, hydrides and GC effluents are the most common gaseous samples. Chemical aspects of volatile species production are discussed in Section 4.3. The reviews quoted there also discuss sample introduction. Aspects of Hg vapour generation and preconcentration are discussed in Chapter 36.

Hydrides can be introduced in an atomizer in different modes [24,25]. In the simplest configuration the generated hydrides and hydrogen are transported immediately to the atomizer, normally by a carrier gas (usually helium or nitrogen). The large dilution effect and kinetic interferences are alleviated by the stopped-flow mode in which the reaction vessel headspace is delayed for a few seconds to allow the generation reaction to complete thus improving the sensitivity and precision. The best sensitivity is offered in the purge-and-trap mode in

which the generated species are cryofocused prior to being conveyed to the atomizer. A U tube (i.d. about 6–7 mm) cooled in liquid nitrogen has usually been used but a straight quartz tube (3.5×65 mm) was found to minimize adsorption losses in ultratrace analysis [26,27].

Different designs of hydride generators have been proposed [28–31]. The batch methods are gradually giving way to continuous-flow or flow-injection procedures. In the continuous-flow mode sample and reagent streams are mixed and the hydride formed separated with a conventional gas–liquid separator [32,33]. It has the advantage of providing a constant output signal as soon as equilibrium is reached but a lower DL compared with batch methods. In FI HG discrete samples are introduced repeatedly with a resultant transient signal to allow for the automation [34–38].

4.2.2 Liquids and solutions

Liquids vary in physical properties in terms of surface tension, viscosity, density and salt content. Whereas few techniques (spectrophotometry, fluorimetry, TXRF) accept liquid samples as such placed in glass or quartz cuvettes or on a special disk holder, most techniques require the liquid to be converted to gas or desolvated aerosol prior to measurement. The most popular approaches for this purpose are nebulization (continuous or discrete) and electrothermal vaporization.

The choice of a nebulizer should be considered in terms of (1) its ability to produce a fine aerosol (all droplets smaller than 4 μm) at a constant rate and size distribution, (2) efficiency of aerosol generation, (3) wash-in and wash-out times (sample throughput and memory effects), (4) tolerance changes in the sample physical properties, (5) susceptibility to blockage and (6) chemical inertness (blank value). The most widely used are pneumatic nebulizers, usually based on the Venturi effect but ultrasonic, high-pressure and direct-injection nebulizers are gaining popularity. Characteristics of different nebulizers have been compared and reviewed [39–46]. Pneumatic nebulizers produce polydispersive aerosols with droplets up to 100 μm which must be removed by a spray chamber which in flame AAS or AES serves for mixing the nebulized sample with the oxidant and fuel gases.

Pneumatic nebulizers which are the most widely used include three basic types: concentric (Meinhard), cross-flow (MAK) and Babington nebulizers. In a concentric nebulizer the sample solution passes through a capillary surrounded by a high-velocity gas stream (argon)

parallel to the capillary axis. They are cheap, robust, offer a good long-term stability and are available in corrosion-resistant versions. The disadvantage is low tolerance to solutions containing higher salt or particulate load because of the small internal diameter of the capillary. Cross-flow nebulizers consist of two capillaries positioned vertically against each other. One of them carries the sample solution and the other the gas stream. The most popular is the MAK nebulizer with fixed positions of the capillaries. They exhibit good long-term stability, high precision (0.5%) and good resistance to blockage even by concentrated solutions (up to 50 g l^{-1}). Corrosion-resistant designs are commercially available. The Babington nebulization principle (blowing a liquid film against a wall causing droplet formation) is applied in the commercial GMK nebulizer. The solution flows in a V-shaped groove within a PTFE base and is blown onto an impacter by a gas flow streaming out of a hole in the groove. As the sample solution is not fed through a narrow capillary, it shows remarkable tolerance to dissolved solids (up to 100 g l^{-1}) and slurries allowing for long-term clog-free operation. The sample uptake is virtually controlled by the pump uptake and may be varied within a wide range. Spray chamber designs have been reviewed [47]. It is usually a barrel-like tube fitted with a drain. Large droplets are removed by turbulent deposition on the inner walls of the chamber or by gravitational action. The common disadvantage of pneumatic nebulizers is their low efficiency (2–10%). It can be improved by a factor of 2 with an impact bead which refines the aerosol. Alternatives aimed at its improvement include fritted disk, ultrasonic, high-pressure and direct-injection nebulizers.

Fritted disk nebulizers involve the aerosol production *via* pumping liquid from an injector tube onto the surface of a fine-mesh-size glass fritted disk, while passing argon through from the other side of the disk [48–51]. It offers low sample consumption (down to $30 \mu\text{l min}^{-1}$) and relatively high nebulization efficiency (*ca* 60%) at the expense of low sample throughput and susceptibility to clogging. It is well suited for organic solvents, e.g. HPLC effluents.

Ultrasonic nebulizers [52–54] show an efficiency of *ca* 40% but the sensitivity is usually seldom increased because of the slowness of nebulization. They are costly and complicated and often unreliable for routine analysis owing to poor stability, reproducibility and low tolerance to dissolved salts and long clean-up time.

Hydraulic high pressure nebulizers are based on pumping the liquid at high pressure through a small orifice onto an impact bead [55,56].

The small and homogeneous size droplets produced can be conveyed to plasma with an efficiency above 60%. It can be adapted to salt-rich solutions [57]. An aerosol deposition module for ETV has been developed [58].

Thermospray nebulizers [59–62] produce an aerosol by passing the solution through a heated capillary. The nebulization is usually followed by the desolvation. Thermospray nebulization for the ICP has been discussed [63,64].

Total injection nebulizers allow large dead volumes and sample loss to be avoided. Microconcentric nebulizer and direct injection nebulizer (DIN) are commercially available and especially suited to FI and HPLC effluents at $30 \mu\text{l min}^{-1}$ [65–69].

Discrete nebulization methods are based on the injection of a small amount of sample into an aqueous carrier stream (driven by means of a peristaltic pump) which is continuously nebulized (cf. Chapter 8) [70–75]. This FI approach offers microsampling capability, shortening the analysis cycle (higher sample throughput) and relative freedom from nebulizer/injector tip blockage and the sampling orifice clogging in ICP MS.

Electrothermal vaporization is based on the production of a dry-vapour aerosol from a microvolume of solution (up to $50 \mu\text{l}$) deposited on a metal filament or graphite rod or in a furnace. In AAS or AFS the vaporization unit acts as an atomizer whereas in other techniques the aerosol formed is conveyed to the atomizer by means of inert carrier gas. These methods yield a transient signal and offer microsampling capability, low background; high sample transport efficiency, high tolerance to organic, high acid and high solid matrices, and a possibility of *in-situ* matrix separation by selective vaporization using temperature programming. The typical drawbacks include incomplete vaporization of refractory elements (which can be alleviated by means of matrix modifiers), and premature losses of volatile elements or compounds. Electrothermal vaporization techniques for atomic spectroscopy have been extensively discussed [76–82].

4.2.3 Slurries

A dilute suspension of ground and sieved powder is either nebulized into a flame or plasma or introduced into an ETV unit. The elemental recovery ($S_{\text{sl}}/S_{\text{sol}}$, where S_{sl} and S_{sol} denote signals from the same concentration of analyte in the slurry and aqueous solution, respectively) is dependent on

the efficiency of leaching the analyte(s) from the slurry as well as on that of the aerosol transport and vaporization of the suspended particles. As the leaching factor is strongly element and sample dependent, it is essential to ensure complete transport and atomization of the solid material, especially as only then can tricky correction factors can be avoided and calibration with aqueous standards is possible.

Small ($<8\text{ }\mu\text{m}$) particles are required for efficient aerosol transport. Babington nebulizers and simple unobstructed spray chambers are recommended to avoid clogging and to improve transport efficiency, respectively. Small organic material particles are easily vaporized even in air- C_2H_2 flame but high temperature plasmas (ICP) are essential for refractory oxides. The permissible slurry concentration depends on the technique used. In terms of nebulization, a concentration of up to 20% dissolved solids is acceptable before serious viscosity effects on the pump delivery rate are encountered. A few percent is acceptable for the inner capillary of the plasma torch whereas only 0.05% is all that can be accepted without blocking the ICP MS orifice. Concentrated slurries can be processed with the use of transient nebulization using FI techniques. The slurry particle size restrictions for ETV techniques are not as severe as for nebulizer systems (20–30 μm).

Slurry sampling is an inexpensive technique which has the inherent ability to reduce time and effort in sample preparation provided that the sample is a powder of small particle size and well-known particle size distribution. If samples need to be ground prior to analysis contamination and fractionation (changed composition) errors are likely to occur. The principles of the slurry technique have been discussed [83–85].

4.2.4 Solid samples

Despite the evident advantage of avoiding often cumbersome and time-consuming sample dissolution, solid sampling is still in its infancy plagued by weighing and homogeneity restrictions and the lack of suitable calibration standards. The practical techniques rely on direct insertion of the sample into the atomizer or conversion of the solid into gas or aerosol (ETV, arc, spark or laser ablation) which is then conveyed to the atomization device.

Direct insertion

This group includes methods in which the sample is directly placed in the atomizer [86–89]. Powders can be inserted directly into a graphite

furnace but residues from refractory metals need to be cleaned up before introduction of the next sample. Usually, samples are placed in a microboat or a small cup which is weighed and then inserted into a flame or electrothermal atomizer. Various aspects of solid ETA AAS [90–93] and ETV ICP MS [94] have been discussed. The sample cup is a conventional undercut graphite electrode used in DC arc emission spectrometry, which on being loaded with a *ca* 10 mg sample is introduced *via* an enlarged central tube into the ICP [95–100]. The sample cup is not consumed as a result of inert Ar atmosphere but consumes a lot of plasma energy so that only volatile elements can be determined. Analysis of materials using direct sample insertion devices has been discussed [101].

Laser vaporization

Interaction of a high-power laser with an absorbing solid leads to strong heating and, consequently, melting, evaporation and explosion generating an aerosol which can be transported to the spatially separated atomizer. In most cases a YAG laser (Y–Al–garnett laser $\text{Y}_3\text{Al}_5\text{O}_{12}$, Nd^{3+} doped) is used. Infrared and UV laser ablation have been compared [102]. The amount of ablated material depends on the laser characteristics and the sample properties and varies from a few μg to a few ng. Laser ablation has been reviewed [103–105]. The technique is best suited for high purity metals and semiconductors for which homogeneous standards for many impurities are available and sample decomposition inadvisable. Pelleted powdered materials (rock, soil) can be analyzed provided that grain sizes are uniform and small and reference materials are available. Dilution with binding material is advised for better homogeneity and improving the absorption coefficient of the target but a contamination danger arises. Laser ablation suffers from the lack of suitable calibration procedures. The ablated amount can be evaluated only by cumbersome measurement of crater dimensions. Otherwise, internal standardization is a valid approach provided that (1) the internal standard is homogeneously distributed, (2) it is affected by matrix interferences in the same manner as the analyte and (3) the signals from the analyte and internal standard are acquired simultaneously. Because of the small ablated amounts laser vaporization should be used with very sensitive detectors. Matrix interferences considerably restrict their use with ETA AAS. It is particularly suited for simultaneous AES [106] and especially ICP MS [107–109].

Arc vaporization

Interaction of an electric discharge with the sample surface creates a plume of vaporized and particulate material, which is transportable in a gas stream into the ICP. These are simple in operation, quite efficient and cheap but poorly reproducible and plagued by matrix effects. These methods are applied to conductive materials and powders of non-conductive samples that are pelletized after mixing with conductive materials [110–115].

4.3 SPECTROPHOTOMETRY

Spectrophotometry is based on the simple relationship between the molecular absorption of UV-VIS radiation by a solution and the concentration of the coloured species in the solution. The technique has been the subject of several monographs and exhaustive surveys [116–122].

4.3.1 Sample and colour systems

As only a few element species (e.g. MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) are capable of absorbing light in the UV-VIS range, virtually all spectrophotometric methods are based on reactions of analytes with colour forming reagents. Organic reagents have been discussed [123] and a comprehensive dictionary is available [124]. Chelating reagents which include numerous compounds from various groups are the most popular.

Inorganic reagents used to form coloured complexes include thiocyanate [Fe(III), Co, Nb, Mo, Re, W, U, Ti], iodide (Bi, Sb, Pd) and peroxide (Ti, V, U). Some elements (As, Si, Ge, V, W, Mo) form yellow heteropolyacids which can be reduced to intensely coloured blue forms.

Dithizone (diphenylthiocarbazon) is a weak acid insoluble in water at $\text{pH} < 7$ but readily soluble in CCl_4 and CHCl_3 . Dithizone reacts with many metal ions to form chelates extracted into the organic phase. The excess of the green reagent is stripped with dilute NH_3aq . The most stable dithizonates (Pt, Pd, Au, Ag, Hg and Cu) are extracted from strongly acid solutions. Some metals (Bi, Ga, In, Zn) are extracted from weakly acid media and others (Co, Ni, Pb, Tl, Cd) from neutral or alkaline media. Some dithizonates are extracted rapidly (Ag, Hg, Pb, Cd) and others are extracted more slowly (Pd, Cu, Zn) while still others (Rh, Ir and Ru) require prolonged heating to be formed.

Azo-compounds contain an azo link between two aromatic rings possessing a hydroxy group in the ortho position. The most important ones include PAN, PAR, Arsenazo III and they generally offer high sensitivity for the majority of transition metals. The bromo- (e.g. 5-Br-PADAP) and chloro-derivatives reach an ϵ value of 10^5 (cf. Sections 4.3.3. and 4.3.4.).

Chelating dyes include triphenylmethane reagents (e.g. Pyrocatechol Violet, Eriochrome Cyanine R, Chrome Azurol S, Xylenol Orange) and xanthene reagents (fluorones, e.g. Gallein, Pyrogallol Red, phenylfluorone and salicylfluorone). They form chelates with most metals. Ionic surfactants (e.g. CTA, CP and Zephiramine) make it easier to dissociate the protons of chelating triphenylmethane reagents and facilitate their reactions with easily hydrolysable metals (Be, Al, Fe(III), Sc, Ti, Zr), leading to very sensitive ($\epsilon > 1 \times 10^5$) but poorly selective methods.

Non-chelating dyes include basic triphenylmethane dyes (e.g. Brilliant Green, Malachite Green, Crystal Violet), xanthene dyes (e.g. Rhodamine B, Rhodamine 6G), and azine dyes (e.g. Methylene Blue, Capri Blue, Meldola's Blue) and acid dyes (e.g. Eosin, Erythrosin). They are intensely coloured and when paired with an oppositely charged analyte ion lead to high sensitivities ($\epsilon > 10^5$).

Crown ethers are not chromogenic unless they contain a chromogen pendant able to dissociate off a proton in a basic medium. The resulting anion interacts strongly with the crown-complexed cation compensating the electric charge. The formation of a *zwitterion* leads to the hydrophobic extractable species (cf. Section 3.1.2) with a considerably shifted absorption maximum compared with the protonated species. Another possibility is formation of an inter- (not intra-) molecular ion-pair with picric acid or an acid dye.

4.3.2 Instrumentation

The basic components of a spectrophotometer include: (1) a light source (usually a tungsten-halogen lamp for the visible range and a D_2 lamp for the UV range), (2) a monochromator (holographic grating) which isolates the desired source emission line, (3) a sample cell, (4) a detector-readout system and (5) a data-processing unit. Instrumentation has been discussed in detail elsewhere [119,120,122].

In single-beam instruments the reference solution and the sample solution are inserted successively into the radiation beam, and the

radiant powers transmitted are measured. As the reference and the sample scans are separated in time accurate measurements are possible only with very stable sources. In dual beam instruments the incident light beam is split by a rotating mirror-chopper into two separate beams, one of which passes through the sample and the other passes through the reference. The same lamp image is thus created at both the reference and the sample photodiodes, thus eliminating time-dependent irregularities in the source, detector and associated electronics. The result is extremely low noise and drift, with the disadvantages of higher cost and loss of 50% of the incident energy.

In the forward optics arrangement the monochromator is placed before the sample cell and the selected wavelength is absorbed by the sample and the transmitted radiation measured by a photocell. In the reverse optics design the sample (and reference) cells are located between the source and monochromator. Radiation reflected from the grating contains all the spectral information simultaneously. It is directed to an array of photodiodes, each of which records a given wavelength. A spectral bandwidth of 1–2 nm is typically obtained.

4.3.3 Measurement and calibration

Spectrophotometric measurements are based on the Lambert–Beer law which describes a linear dependence of absorbance A (defined as the negative logarithm of the fraction of light emerging from the sample) on the concentration c and the path length b of radiation within a sample: $A = \log(I_0/I) = abc$, where I and I_0 are the intensities of the emerging and incident beams, respectively. The constant a is the absorptivity which is usually written as ϵ (molar absorptivity) if c is expressed in mol l^{-1} . The method of calibration graph is the most popular for calibration (*cf.* Section 5.1).

In the majority of methods the absorbance of a test sample is measured against a reagent blank. In *differential spectrophotometry* the absorbance is measured against a standard of known concentration. In analog *derivative spectrophotometry* the absorption spectrum is differentiated and the amplitude peak-to-peak or peak-to-zero is taken as a measure of absorbed light [125]. In *solid-state spectrophotometry*, the analyte is sorbed as a coloured complex on a solid support (or made to react with the support load to form a coloured species), and the absorption of the support is measured [122].

4.3.4 Analytical characteristics

Sensitivity, precision and dynamic range

The sensitivity is characterized by the molar absorptivity (ϵ ; $\text{l mol}^{-1} \text{cm}^{-1}$), and the specific absorptivity ($a = \epsilon/(\text{atomic weight} \times 1000)$). For most methods ϵ is in the range 1×10^4 – 1×10^5 . Assuming the minimum measurable absorbance of 0.01 and a light pass of 1 cm the lowest determinable concentration is $1 \times 10^{-7} \text{ M}$, i.e. 5–20 ng ml^{-1} in a 1 ml cuvette). Experimental sensitivity is usually increased by 1–2 orders of magnitude in extraction, flotation and solid-state spectrophotometric methods owing to intrinsic preconcentration. The precision is the highest when absorbances of 0.4–0.5 units are measured and varies from 0.5–2%. By the differential method a precision of 0.2–0.5% is obtainable, which enables macroquantities to be determined.

Selectivity and interferences

The selectivity of a method depends on the reagent used, the pH of the medium, and the nature of the complexing agents used to mask interfering ions. Efficient control of these factors compensates for the paucity of specific reactions. In addition to interferences from concomitant elements, others due to the absorption of the reagent and unspecific absorption due to turbidity may be present. Spectral interferences can be alleviated by mathematic treatment (derivative spectrophotometry and principal component analysis) to resolve the overlapping spectra. Non-spectral interferences are associated with poor time stability of the coloured complex so that the absorbance must be measured at the fixed time interval from the beginning of the colour reaction. Some colour reactions are temperature and pH sensitive. Competitive reactions in the system and too great a variation in ionic strength in the sample solution can affect the colour reaction, too.

Versatility, cost and turnover

All metals and metalloids can be determined in solutions in concentrations down to the ng/ml level (after preconcentration). Instrumentation is available in virtually all price categories depending on the degree of sophistication. Analysis requires profound knowledge of chemistry of elements. Sample throughput may be very high in *on-line* systems (FIA) for trace elements in water and simple matrices (*cf.* Chapter 7). Spectrophotometry is still the method of choice for some metalloids (e.g. B) (*cf.* Chapter 19).

4.4 ATOMIC ABSORPTION SPECTROMETRY (AAS)

This technique is based on the fact that ground state atoms produced in an atomizer absorb radiation at element characteristic wavelengths in proportion to their concentration. Various types of atomizers, usually flame, quartz or graphite furnace, lead to virtually different analytical techniques, complementary rather than competing. Regardless of the atomizer used AAS techniques enjoy some common features. A separate line source is needed for each element to be determined. Simultaneous AAS is still in its infancy [126–128]. Isotopic analysis is possible in a very limited number of cases (Li, B, Pb, Hg and U, provided that highly enriched isotope sources are available). The unique lock-and-key effect makes the atomic absorption mechanism strongly element-specific, eliminating in principle spectrum overlap interferences. Fundamental aspects of AAS have been widely discussed in monographs and review articles [129–140].

4.4.1 General

The basic components of an AAS spectrometer are similar to those of a UV-VIS spectrophotometer (*cf.* Section 4.3.2) and are discussed in detail elsewhere [129,130,138]. As the user has usually the choice concerning the radiation source, the type of the atomizer and background correction, these features are discussed below in more detail.

Radiation sources

Line-like sources emitting the element characteristic wavelength are required. The radiation is produced from a vapour of the analyte element. The principal sources include hollow cathode lamp (HCL) and electrodeless discharge lamp (EDL). Hollow cathode lamps are fairly cheap, bright and stable light sources but they have poor intensity in the UV region and short lifetime for volatile elements. Electrode discharge lamps offer much stronger radiation intensity (in particular for easily vaporizable elements) which results in considerable improvement in signal-to-noise ratio and hence higher precision and sensitivity, especially in the UV range. The operating life of EDLs is longer than that of HCLs but they are notably less stable, require a warm-up time of up to 30 min, and are available for a limited number of elements. In principle, an individual radiation source is needed for each element to be

determined. Multielement sources are available for some combinations of elements. They are more expensive than single-element lamps and particularly suited as backup sources for occasionally needed analyses.

Background correction

The analyte-specific absorption can be increased in a non-specific way by background absorption due to light scattering on particulates formed or present in the light path (e.g. by recombination of sample matrix at cold spots) or due to broad-band molecular absorption caused by molecules, radicals, or molecular ions formed or vaporized in the atomizer (e.g. from the alkali and alkaline earth halides). The amount of incident radiation thus absorbed or scattered must be subtracted from the total measured absorbance in order to obtain the net absorbance of the analyte atoms only. The most popular is the continuum source method in which the non-specific absorbance is measured with a continuum radiation source (e.g. a D_2 arc lamp). It is averaged over the bandpass of the spectrometer (typically 0.2–0.7 nm), and subtracted from the total absorbance measured at the main resonance line of the element with a line-like radiation source. The method is relatively simple and inexpensive but fails if the background exceeds 0.5 units. Other disadvantages include an elevated noise, overcorrection if an emission line from another element present in the sample falls within the monochromator bandpass, and the inability to correct background attenuation of electronic excitation spectra consisting of many narrow lines. The method is restricted to lines below 400 nm unless a tungsten-halogen lamp is used. Other methods include the Zeeman effect and Smith–Hieftje background correction. The detailed description of operational principles is beyond the scope of this book and can be found elsewhere [130,141]. The advantages of ZAAS include the need for one light source only for any wavelength, and the measurement of the background absorption at a wavelength very close to the analyte one (direct ZAAS) or exactly at the same one (inverse ZAAS). High non-specific absorbances (up to 2 units) and highly structured backgrounds can be corrected for, while a sensitivity loss of 10–30% and a decrease in linear range must be taken into account. The advantages of the Smith–Hieftje method are similar. The system is cheaper; however, it is difficult to incorporate it into the existing spectrometers. In addition, the sensitivity is reduced and so is the lifetime of the HCL for the more volatile elements.

Calibration

Quantitative measurements in AAS are based on Beer's law which states that concentration is proportional to absorbance: $c = kA$ (*cf.* Section 4.3.3). Calibration with matrix matched standards is usually required. The method of standard additions is generally preferred to the calibration graph. Microprocessor-controlled modern instruments are capable of calibrations using non-linear calibration graphs [142]. The calibration process is usually automated in FAAS using flow-injection techniques. The transient shape of GF AAS signals can be monitored in peak height or peak area mode. The former usually gives better sensitivity and the latter better precision and larger freedom from interferences. Peak area integration can eliminate variations in the atomization rate caused by different compounds of the same element (volatilization interferences).

4.4.2 Flame atomic absorption spectrometry

Atomizer

A flame is used both to atomize the sample and to maintain a cell of atomic vapour within the light path of the instrument [143,144]. An air-C₂H₂ flame (2000–2500°C) is usually used for readily atomized elements but it is inadequate for refractory elements or those forming thermally stable oxides or carbides. The alternative more energetic N₂O-C₂H₂ flame (*ca* 3000°C) causes an appreciable shot-noise problem and is generally more difficult to work with. The low temperature air-H₂ flame (2000°C) is vulnerable to matrix interference and used only if gaseous samples are introduced. The sample solution is usually converted into an aerosol mist (in a pneumatic nebulizer, *cf.* Section 4.2.2) and mixed with the oxidant and fuel gases. Modern instruments have a precise and safe fuel-oxidant mixture regulation system which is essential to achieve good precision. The performance of a flame atomizer is characterized in terms of nebulization efficiency, drop-size distribution of the aerosol entering the flame and level of fluctuation of the analytical signal. More detailed criteria have been reviewed in detail elsewhere [145,146].

Sensitivity, precision and dynamic range

Flame AAS offers low DLs (down to ng ml⁻¹) for some elements (Li, Na, Ca, Ag, Cu, Cd, Zn, Mn) with more than 60 elements measurable in the 0.01–1 µg ml⁻¹ range (*cf.* Fig. 4.1). The sensitivity is hampered by

Actinides

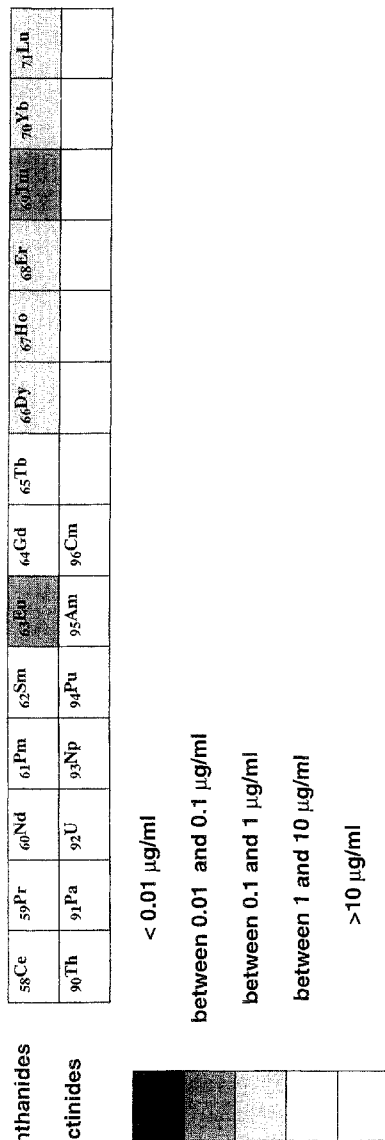


Fig. 4.1. Detection limits in flame AAS.

inefficient nebulization and can be improved by the introduction of the sample as a solution in a suitable organic solvent (e.g. MIBK) or total consumption nebulizers. Long term precision is likely to be within limits of 3–5% while short-term precision is 1–3%. The dynamic range of 1–2 decades is small compared with other atomic spectrometric techniques.

Physical interferences are associated with differences in the nebulizer uptake rate and nebulization between sample and standards which depend on the viscosity, total salt content, acidity, the length of the capillary and the depth of its immersion. They are controlled by matrix matching or dilution of the sample.

Ionization interferences are due to a decrease in the population of free atoms because of the ionization in hot flames and result in reduced absorbances measured (chiefly for alkali and some alkaline earth metals). They are prevented by the addition of a large excess of an element (usually Cs) that is more readily ionized (ionization buffer) and thus provides electrons capable of recombination of the analyte ions formed beforehand.

Chemical interferences are due to the formation of thermally stable compounds in the flame by the analyte (e.g. refractory phosphates, oxides or carbides), thus hampering its atomization. In some cases a highly refractory compound formed by the matrix can trap (by occlusion) the trace analytes resulting in the same effect. These interferences can be overcome by the use of a hotter flame, releasing agents (forming a more volatile compound with the analyte than the interferent, e.g. La vs $\text{Ca}_3(\text{PO}_4)_2$) or sequestering (shielding) agents (which prevent the reaction between the analyte and interferent, e.g. EDTA which complexes Ca but does not retard atomization).

Emission interferences are due to the increase in the photomultiplier's electronic noise caused by high radiation emission falling within the spectral bandpass used which occurs for some elements (Ca, Ba) in hot flames. They result in degraded precision and can be alleviated by decreasing the slit width, diluting the sample or using a cooler flame.

Spectral interferences include non-specific element, molecular absorption and light scattering interferences which enhance the AAS signal. Molecular absorption can be reduced by means of hotter flames able to break down the absorbing species. Background correction is recommended for measurements below 300 nm using D_2 or the Smith-Hieftje method.

Versatility, cost and turnover

Flames are convenient to use, reliable and relatively free from memory effects. Burner systems are small, durable and inexpensive. The signal-to-noise ratios obtained are sufficiently high to allow adequate sensitivity and precision to be obtained in a wide range of analyses in the range 190–900 nm. Flame cells are only rarely able to atomize solid samples and viscous liquids directly. The systems are poorly transportable owing to the need for high-pressure cylinders and fuel gas and the need for an open flame sometimes cannot be reconciled with unattended operation. The cost of a modern flame AA spectrometer reaches \$20,000–30,000. Sample throughput of *ca* 20 samples h⁻¹ can be enhanced by FI sample processing (*cf.* Chapter 7).

4.4.3 Graphite furnace atomic absorption spectrometry

Atomizer

This is a graphite tube placed in the light beam of the spectrometer and heated by a high intensity electrical current [133–139]. The sample is usually deposited as a solution (1–50 μ l in volume) onto the inner wall of the tube. The atomic vapour generated when the furnace is fired absorbs light from the lamp giving rise to a transient absorbance signal. Graphite tubes are made of spectrally pure, high density graphite. They may be used bare (uncoated), coated with a thin layer of pyrolytic graphite, or pre-treated with suitable carbide-forming elements. Coated tubes enjoy an extended lifetime and are used for refractory and carbide-forming elements (B, Mo, Ti, U, V). The L'vov platform is a small plate of massive pyrolytic graphite of high thermal anisotropy inserted into the graphite tube. Its purpose is to delay atomization of the sample until the graphite tube and the inert gas have reached thermal equilibrium.

Graphite furnace programme

In GF AAS desolvation of the sample, dissociation of the analyte from the matrix and generation of analyte ground state atoms are separated in time: this is realized by graphite furnace temperature programming. The programme includes a drying step (*ca* 100–150°C) in which solvent is removed, charring (*ca* 300–500°C) in which the matrix is broken down and volatilized off and an atomization step (usually 2000–3000°C) in which element vapour is generated. During the last step the internal Ar stream is stopped. The choice of the temperature and time programme depends on the volatility of both the analyte and the matrix and needs

to be optimized for a given application. Modern instruments offer a maximum power heating (2000°C) option which is essential for the analysis of refractory elements as it lowers the atomization temperature and in the STPF concept (see below).

Matrix modification

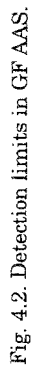
Matrix or analyte modification is the addition of a reagent (modifier) to convert the analyte element into a phase of higher thermostability and/or to increase the volatility of concomitants. The aim is to permit high enough pyrolysis temperatures to remove the bulk of the matrix during thermal pretreatment of the sample without using any analyte element prior to the atomization step. Effective analyte or matrix modification greatly reduces the number of spectral interferences due to overlapping molecular or atomic lines of concomitants and scattering by non-volatilized particles. It is important part of the STPF concept (see below). Matrix modifiers include metal salts (Ni, Cu, La, NH_4NO_3 , phosphates) and some organic salts (ascorbic acid, citric acid, EDTA or thiourea) and have been extensively discussed [147–151]. The most favourable is apparently a mixture of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ [148]. It is capable of stabilization of numerous elements to high pyrolysis temperature (>1000°C) and creates no problems with excessive background attenuation and lifetime reduction of graphite tubes and the availability of Pd and its compounds in high purity. Matrix modifiers for particular elements are discussed in detail in Part III.

Stabilized temperature platform furnace

The STPF is a concept devised by Slavin aimed at interference-free analysis [152]. It involves the use of platform atomization, maximum power heating, minimal temperature difference of 1000°C between charring and atomization, gas stop during atomization, matrix modifiers, maximum heating rate, peak area integration and usually Zeeman background correction. Only the fulfilment of all these conditions leads to absolute minimization of interferences.

Detection limits, precision and dynamic range

Excluding MS, GF AAS is the most sensitive analytical technique for routine analysis in terms of ADLs which are 2–3 orders of magnitude lower than in FAAS (*cf.* Fig. 4.2). This is due to the fact that, during atomization, the atomic species are concentrated for a period of up 0.5 s within the optical path of the instrument. Graphite furnace AAS



exhibits relatively poor precision because of the small sample size and, often, interferences. The dynamic range is practically restricted to 1 decade.

Interferences

These are common in graphite furnace AAS especially when complex matrices are analyzed. Physical interferences are enhanced by the small sample volume introduced when pipetting viscous, highly acidic or high-salt content solutions. Dilution, matrix matching and standard addition are used to overcome these effects. Chemical interferences include matrix dependence on the volatilization rate (and hence signal height), loss of analyte prior to atomization and formation of refractory compounds. The matrix effect can be minimized by addition of a modifier, selective volatilization of matrix components in the charring step, signal integration and the method of standard additions. The latter often fails owing to the mismatch in the analyte form added and actually present in the sample. Loss of analytes in the drying or ashing step is due to the formation of volatile compounds. It is particularly acute for Se, Cd, Zn, Pb, As, Te which need to be converted into more stable species by means of a suitable modifier. Some elements may form refractory carbides by reacting with the graphite tube surface. Spectral interferences associated with background effects are acute especially in the UV range. Light scattering is caused by particles condensing at the cooler ends of the GF, or by the release of graphite from the furnace wall at high temperatures. Non-specific molecular absorption is caused by matrix components (usually alkali halides) absorbing at the analyte line at the atomization stage. Zeeman background correction is recommended.

Versatility, cost and turnover

Graphite furnace AAS is an ideal technique for ultratrace determination of *ca* 60 elements (down to 10 pg in 10–50 μ l of sample). For volatile metallic elements, such as Cd, Cu, Pb and Tl, direct atomization from finely powdered solid samples or suspensions, may be possible. Direct analysis of solid samples is possible. The use of the STPF concept considerably reduces the interferences and also in relatively complex matrices. The disadvantage is monoelement analysis and relatively long time per determination. Modern instruments equipped with an autosampler tray can work unattended. The cost of a GF atomizer is *ca* \$15,000 in surplus of an AA spectrometer which is within a reach of even relatively small laboratories.

4.4.4 Quartz furnace atomic absorption spectrometry

The *quartz furnace atomizer* is a quartz tube, positioned in the light beam of the spectrometer and heated either by flame or electrically by a coiled wire. The system is available commercially in different dimensions as the MHS-20 or FIAS quartz furnace. Gaseous samples are required. Quartz furnace AAS is used for the high sensitivity determination of mercury and the hydride-forming elements such as As, Se, Sb, Te, Bi and Sn, and as an element-selective detector for GC [153] (see Part III). The sensitivity of commercial devices is a factor of 10 poorer than in the graphite furnace technique but a careful optimization of operating conditions in self-made systems allows comparable or even lower values to be obtained.

No interferences due to background attenuation occur provided that hydrogen is not allowed to ignite at the open tube ends. Otherwise, background correction is recommended since variations in the transparency of the flame may occur. As the analytes are separated from the matrix prior to being swept into the atomizer chemical interferences are virtually absent since a relatively small number of components are present in the atomizer.

4.5 ATOMIC EMISSION SPECTROMETRY

Atoms and ions formed in a high temperature environment are excited by the absorption of thermal energy. Returning to the ground state they emit photons at element-characteristic wavelengths. The light intensity is proportional to the concentration of atoms present which is the basis of quantitative atomic emission analysis. A typical AES system consists of (1) an energy medium for atomization and excitation of the test sample, (2) a dispersive unit which isolates the various wavelengths of light emitted and (3) a measurement-readout device. Emission spectrometric techniques are divided according to excitation source which may be a flame, arc discharge or plasma (luminous very hot gases in which more than 1% of the atoms are ionized). The choice of the excitation method depends on the material to be analyzed and elements to be determined. Arc discharge sources, once very popular, have practically disappeared from modern laboratories giving way to various plasmas. The most common analytically used plasmas include inductively coupled plasma (ICP), direct current plasma (DCP) and microwave-induced plasma (MIP).

The test sample is usually a liquid introduced as aerosol on nebulization and desolvation. Gaseous (introduced directly) or solid samples (introduced as slurry on nebulization or on electrothermal or laser vaporization) can be analyzed (*cf.* Section 4.2). The tolerance to sample load depends on the energy supplied by the source. The MIP does not accept anything but gases whereas even concentrated slurries of refractory materials can be fed into an ICP.

4.5.2 Flame atomic emission spectrometry

The technique is based on the measurement on the radiation from an atom excited in a flame. The $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame is the most widely used but diffusion hydrogen flames are preferred for gaseous samples.

Instrumentation and measurement

A nebulizer and burner assembly exactly the same as that used in FAAS can be used. In the simplest configuration a bandpass transmission filter is used to isolate the analyte-characteristic emission line. Modern instruments include a monochromator in a set-up similar to that used in AAS with the exception of an external radiation source which is not required in AES. Generally atomic absorption instruments can be operated in the emission mode. The wavelength scanning option is essential when the baseline is likely to change from sample to sample and when the spectrum is very complex. Fixed wavelength instruments are recommended for routine analyses. The concentration measured must be corrected for the background. Calibration is done either by a calibration graph (usually prepared with matrix-matched standards) or by the method of standard additions.

Analytical characteristics

Detection limits in flame AES are generally comparable with those of flame AAS but the AES method is more sensitive for Al, Ba, Li, K, Na and V. Short-term precision below 1% can be obtained. The dynamic range is between 1 and 2 decades and is restricted by self-absorption (absorption of part of the light emitted in one part of the flame by ground state atoms in another part of the flame). Flame AES is fairly prone to interferences. Matrix, ionization and chemical interferences are similar to those observed in FAAS (*cf.* Section 4.4.2) whereas

spectral interferences are more important. Nearby-line interferences are due to a line of another element in the sample falling within the spectral bandpass of the monochromator and are relatively rare. Background molecular radiation produced by molecules of the flame and others present in the sample, however, is common. Molecular emission background can change from sample to sample and can be corrected for by a measurement at each side of the analyte line.

Versatility, cost and turnover

Flame photometry is particularly useful in determining $\mu\text{g ml}^{-1}$ amounts of alkali and alkaline earth metals in solution. Many compounds such as refractory oxides or carbides cannot be reliably determined even with an $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame. Gases (e.g. GC effluents) are analyzed for Sn. The instruments for routine measurements of the Na-to-K ratio in biomedical samples are relatively inexpensive as the emission lines, 589 nm and 766 nm, respectively, are selected by means of cheap transmission filters. Applications can be extended to the determination of other alkali metals such as Li, Cs and Rb at trace levels at the expense of the need for a monochromator to reduce the spectral interferences and, consequently, increase in price to the level of an AA spectrometer. The turnover is comparable with that of FAAS but the operation is simpler as no radiation source is required. Unlike AAS, FAES has the inherent capability for simultaneous multielement analysis.

4.5.3 Inductively coupled plasma atomic emission spectrometry

An ICP is a plasma sustained in a quartz torch placed in a radio frequency (27.12 MHz) oscillating magnetic field. Argon is chosen as the plasma gas for its inertness, optical transparency in the UV-VIS part of the spectrum, high first ionization energy (all elements can be determined) and moderate low thermal conductivity, so that heat is retained within the plasma fireball, sustaining stable operation of moderate power inputs. The temperature in the plasma reaches up to 8000°C . The vortex flow of coolant gas prevents the torch from melting. General and analytical aspects of ICP have been reviewed [154–166].

Instrumentation

Apart from the sample introduction system discussed in Section 4.2, other instrumental components of particular concern for an ICP user

are the torch and the spectrometer as they directly affect the analytical performance and the cost of the system. Advanced evaluation of all the components of an ICP spectrometer can be found elsewhere [167–169]. The principal torch designs are the Greenfield and the Fassel torches. The torch consists of three concentric cylinders which are channels for (from the inside) the sample carrier gas ($\sim 1 \text{ l min}^{-1}$), the plasma gas flow (10 l min^{-1}), and the coolant gas flow. In the Greenfield torch, nitrogen is the outer gas and argon the intermediate and carrier gas. The Fassel torch is narrower. Only two argon flows, outer and carrier, are used with organic-free aqueous solutions, whereas three Ar flows are necessary for organic and organic-rich liquids. Although similar DLs are obtained with the Greenfield and Fassel torches, the former requires higher RF powers and higher gas flows than the smaller diameter Fassel torch. The latter shows less tolerance to solutions of high solute contents, and it has a greater tendency to be extinguished by ingress of air into the nebulizer. Guidelines for the evaluation of the ICP source have been given [170].

The dispersive unit relies almost exclusively on the use of diffraction gratings. The standard is a low resolution holographic grating with *ca* 1800 lines cm^{-1} and resolution of 0.018 nm operating over the range 160–800 nm. High resolution instruments use two holographic gratings, one with 1800 and a second with 3400 lines cm^{-1} , and operate in the range 160–400 nm. Selection is made by a microprocessor based on the wavelength to be monitored. A scanning monochromator is programmed to move sequentially to the desired emission wavelength where it pauses briefly to allow a satisfactory emission signal to be recorded. A simultaneous instrument uses multiple detectors along the focal plane of a fixed, concave diffraction grating so that the various signals are measured at the same time. The movable entrance slit enables the optical path to be moved slightly with respect to the detector, creating a small scanning effect enabling background procedures. The figures of merit to be considered when choosing a monochromator [171] and a polychromator [172] were discussed. Image detectors capable of producing a whole emission spectrum from a sample at a very high resolution are likely to invade the market in the near future [173,174].

Measurement and calibration

A measurement is preceded by the choice of the analytical wavelength and optimization of operating conditions [175–178]. The most

important parameters include forward power, the observation height and injector gas flow rate which are interdependent and require an optimization strategy, e.g. a simplex strategy [179]. Intermediate and outer gas flow rates in the torch and the solution uptake rate are usually optimized independently. The most common optimization functions include intensity, net intensity, signal-to-noise ratio, signal-to-background ratio and signal-to-background noise. In multielement analysis the optimization is usually carried out for elements at the levels close to the DLs whereas others are optimized under suboptimum conditions. More objective is the optimization of a combined response consisting of a weighted mean of the individual element responses [180]. For routine applications commercial instruments include packages with recommended conditions for various types of analyses which, when followed, produce satisfactory results. Analysis by ICP AES is usually based on a steady signal and a few millilitres of sample is required for a single measurement. Lower amounts (a few to several microlitres) of samples are sufficient when transient signals are registered (FIA, ETV). Calibration is usually performed using a standard curve prepared with matrix-matched solutions, by the method of standard addition and, when a polychromator is used, by internal standardization (*cf.* Chapter 5).

Figures of merit

Detection limits are in the 0.1–100 ng ml⁻¹ range when conventional nebulization is used and are summarized in Fig. 4.3. They are element dependent and lower than in FAAS. Experimental DLs can be improved using more efficient nebulization or alternative sample introduction techniques, e.g. hydride generation (*cf.* Section 4.2). The sensitivity is proportional to the integration time and baseline noise to the square root of the integration time so the DL is inversely proportional to the square root of the integration time. Little difference is noted between DLs obtained by simultaneous and sequential instruments when the same lines and comparable integration times are used. Detection limits are degraded in concentrated solutions and in the presence of organic solvents. The precision is dictated by the noise of the nebulizer and is between subpercent to a few per cent at the level 100 times the detection limit. In practice it is fairly independent of the integration time. The linear range is very large (over 4–5 orders of magnitude) due to minimal self-absorption of radiation.

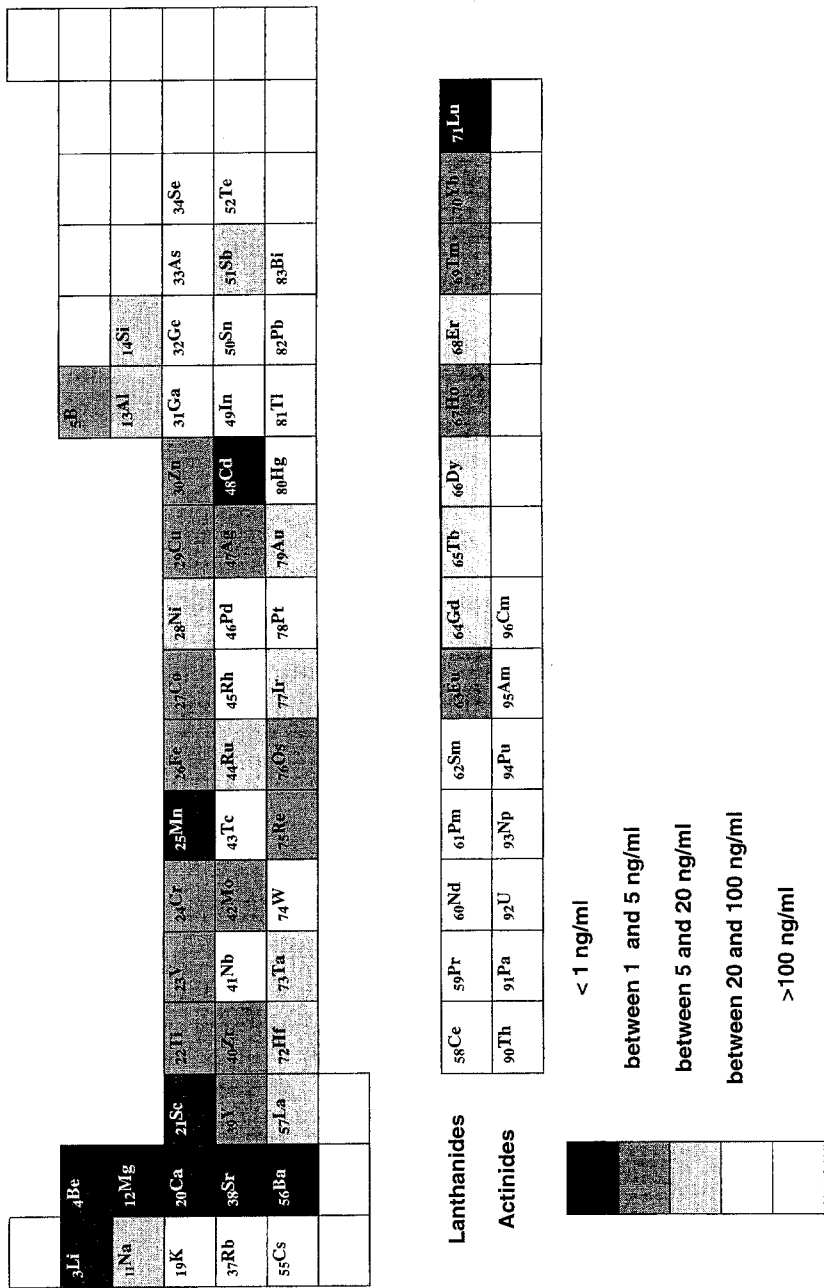


Fig. 4.3. Detection limits in ICP AES.

Selectivity and interferences

Nebulizer interferences are caused by alterations in the salt, acid or organics content in the nebulized solution due in the viscosity, surface tension or solution density [181–186]. Clogging of the nebulizer with carbon or salt during prolonged nebulization of organic or concentrated solution, respectively, decreases the sensitivity. Memory effects are not uncommon if samples with significantly different concentrations are analyzed and long tubes and large vessel surfaces are used. Differences in volatility between matrix and the analyte in the desolvation chamber result in apparent signal enhancement and decreased precision [187]. These effects can be overcome by matrix matching, *on-line* dilution or FI techniques. Chemical interferences are virtually absent in ICP AES as even very thermally stable species are efficiently ionized. Plasma-related matrix interferences are caused by high concentrations of ions, acids and organic solvents and especially affect analyte lines with high excitation potentials [188–193]. Spectral interferences are serious because of fairly complex line-rich spectra that result from high temperature excitation [194]. Broad-band overlaps seldom occur owing to the virtual absence of molecular species in the plasma. High resolution monochromators cannot overcome line coincidences and broad-band overlaps (*cf.* Ref. [195]). Base-line shifts due to Al, Fe, Ca and Mg in some regions are common. Background correction by scanning the vicinity of the line and subtracting the background signal is essential. The standard addition method is useless to correct for spectral interferences. Valid methods include fairly cumbersome separations or chemometric approaches such as Kalman filtering [196] or the use of orthogonal polynomials [197].

Versatility, cost and turnover

Inductively coupled plasma AES can be successfully used for the determination of virtually all metals but analysis for trace alkali metals may be problematic. The simultaneous multielement capability is high at the expense of sensitivity losses of a factor of 2–3 at compromise conditions. Because of the large dynamic range measurement of major and trace elements within the same run is generally possible. The investment cost is fairly large (*ca* \$100,000) as are the running costs as a result of large Ar consumption, even with smaller Fassel torches. The higher cost of a polychromator is offset by the reduction in time required to determine several elements. The modern instrumentation is capable of ten multielement determinations per hour (in simultaneous mode) on unknown samples.

4.5.4 Other atomic emission techniques

Direct current plasma atomic emission spectrometry

The most popular (commercial) design is a three-electrode DC plasma. Plasma gas (argon, 6–8 l) is heated by a dead current passing between a tungsten cathode and two graphite electrodes. Analytical features are similar to those of ICP (low detection limits, high precision, good stability and three orders of magnitude dynamic range). The instrumentation is simple and less expensive than that for ICP AES; solutions with a high salt content can be analyzed. The disadvantages include the need to change the anodes frequently, extremely small excitation region favourable for analysis, difficulties in achieving optimum conditions for multielement analysis and interferences from alkalis. DCP is chiefly used as an element-selective detector in gas and liquid chromatography [198].

Microwave induced plasma atomic emission spectrometry

The method is based on an electrodeless discharge generated in a quartz capillary tube having an inner diameter of a few millimetres placed in a resonant cavity (a hollow metal container having a shape and size which allow a standing electromagnetic wave to be established within or along it). Atmospheric pressure MIP is obtained in a TM_{010} cavity designed by Beenakker. It is commonly operated with a relatively small microwave generator (2.45 MHz) capable of delivering a power of 200 W to the plasma. The gas flow is *ca* 0.1 l min⁻¹. The low power makes this inappropriate for solution and solid analysis. An MIP spectrometer is an excellent detector for GC capable of detecting virtually all metals and metalloids [199,200]. Detection limits offered reach the subpicogram level for many elements including Hg, Sn, Pb and picogram levels for most of the others [201–204]. Separative column atomizer MIP AES has been developed [205].

4.6 FLUORESCENCE SPECTROMETRY

Fluorescence methods are based on the absorption of energy by a molecule or an atom, and re-emission of this energy at the same (resonance fluorescence) or longer (Stokes fluorescence) wavelength while returning to the previous state. The amount of the emitted energy (fluorescence) is measured. The fluorescence intensity is proportional to the intensity of the exciting radiation. Depending on the electrons

excited fluorimetric techniques can be divided into three basic categories: molecular fluorescence spectrometry (electrons from molecular orbitals), atomic fluorescence spectrometry (electrons from outer shells) and X-ray fluorescence spectrometry (inner core electrons). The techniques differ considerably in terms of sample analyzed, instrumentation required and analytical characteristics obtained.

4.6.1 Molecular fluorescence spectrometry (spectrofluorimetry)

A sample, exposed to radiation of one wavelength absorbs this radiation and re-emits radiation of the same or longer wavelength. A re-emission occurring in about 10^{-9} s is called fluorescence whereas a re-emission after about 10^{-6} s or more is called phosphorescence. Both terms tend to be replaced by the more general term luminescence. Photoluminescence denotes the relaxation of molecules excited by photon absorption whereas the term chemiluminescence is used when the excitation is the result of a chemical reaction. General aspects of spectrofluorimetry have been discussed [206–208].

Sample and fluorescent systems

Since only a few simple inorganic ions (U(VI), Ce(III), Tl(I) and some of the lanthanides) exhibit measurable fluorescence, most of the methods for elements are based on the formation of a fluorescent species, usually by chelation with a fluorophore. The most versatile fluorophores include 8-hydroxyquinoline (Ag, Al, Ca, Cd, Ga, Mg, Mn, Sn, Zn), morin (Al, B, Be, Cd, Ga, Pb, Sn, Th, U, Zr) and rhodamine B (Al, Au, Ga, Tl, W). Selectivity is controlled by the pH of the reaction medium and masking. Solids can also be analyzed by fluorescence. The yellow fluorescence of compounds of uranium allows its detection in ores on their fusion, e.g. with sodium fluoride.

Instrumentation and measurement

The components of a fluorimeter are essentially the same as those of a spectrophotometer but the fluorescence is measured at an angle to the light beam to avoid measuring any transmitted radiation. A more intense radiation source is needed which is usually a mercury arc. In the case of the simplest filter fluorimeters the incident and fluorescence wavelengths are isolated by means of a bandpass filter. Gratings are used for the same purpose in newer designs. Resolution is thereby improved, the spectral interferences being considerably reduced.

Analytical characteristics

Fluorimetry is considered to be complementary to spectrophotometry. It offers a lower DL because of the virtual absence of background signal at an angle to the incident beam where fluorescence is measured. The dynamic range is fairly narrow so very dilute solutions are usually required for analysis. Fluorimetry also offers higher selectivity but is more vulnerable to interferences. An increase in temperature results in a decrease in fluorescence. pH affects the acid–base equilibria of fluorophores and thus their reactivity. Paramagnetic substances (with a triplet ground state) promote the opportunity for radiationless relaxation of other molecules, potentially fluorescent. Fluorimetry is generally unsuccessful for the determination of larger concentrations because of self-absorption and self-quenching. Indirect methods based on fluorescence quenching are fairly popular.

4.6.2 Atomic fluorescence spectrometry (AFS)

Atomic spectroscopy involves energy transitions between outer electron orbitals, such transitions being induced by the excitation of outer electrons to a higher energy state, without ionization. AFS utilizes the same basic components as AAS in a different optical arrangement. The light source is placed at a right angle to the optical axis. The sample may be gas, liquid or solid provided that a suitable introduction system, as described in Section 4.2, is employed.

Radiation sources

The sensitivity is directly proportional to the source intensity so electrodeless discharge lamps are the usual choice. A broadband continuum source (xenon lamp) can be used, eliminating the need to change the source for each element determined. Lasers offer high intensity monochromatic and coherent radiation but are expensive and have limited wavelength range (217–900 nm). For many elements measurements can be done at lines other than resonance lines. The use of an ICP fed with a concentrated analyte(s) solution provides an attractive quasi-monochromatic radiation source [209,210].

Atomizers

Air–C₂H₂ and N₂O–C₂H₂ flames shielded by N₂ or Ar gases (to reduce background emission) are used but suffer from chemical interferences discussed in Section 4.4.2. Hydrogen flames are recommended because

of their low background emission but their use is restricted to gaseous analytes. A graphite furnace is a suitable atomizer as, when an inert gas atmosphere is used, the fluorescence quenching is minimized without loss of atomization efficiency. On the other hand, the strong emission of the hot graphite tube increases the background. In general, the ETA method is more time consuming and expensive than the flame method. It is recommended for lower sample amounts and concentrations, especially if laser excitation is used [211,212]. Electrothermal QF atomizers proved especially efficient for gaseous species. An ICP plasma is an efficient atomizer offering minimum light scatter and chemical interferences [213,214]. Solid samples can be analyzed. Plasma emission is made negligible by viewing plasma considerably above the coil (45–66 mm). A tandem system, in which one ICP fed with a concentrated multielement standard solution serves as a radiation source while another one acts as an atomizer for a sample solution, has been described [215,216]. This system, called atomizer, source, ICPs in AFS (ASIA), offers an attractive approach to remove spectral interference in complex samples without the need for an expensive, high resolution monochromator [215,216].

Instruments

Non-dispersive instruments employ line-like sources specific for the analyte element [217]. The signal intensity is directly proportional to the incident intensity, space angle, quantum yield and transmission efficiency of the optics. Advantages include simplicity and low cost. Optical transmission is not limited by the presence of a monochromator. In multielement analysis rotating filters may be employed to separate the wavelengths of different elements from each other. Non-dispersive instruments are prone to interferences by stray light and background emission from the atomizer. Therefore, shielding of flames with N₂ or Ar gas is required.

Dispersive instruments employ monochromators for wavelength selection. For a continuum source a high resolution monochromator is required. As the exit slit width is narrower than that in a non-dispersive instrument, thermal background emission and stray light originating from the atomizer can be considerably decreased but at the same time the optical transmission also decreases.

Analytical characteristics

The DL is affected by the detector noise, background emission of the atomizer and molecular fluorescence. Detection limits with a contin-

uum source are poorer than with line sources. The linear dynamic range can vary from 3 to 8 orders of magnitude. Precision of a few percent is a standard. Matrix interferences are due mostly to light scatter from particles present in the atomizer, and molecular fluorescence of matrix compounds. Matrix matching is recommended. Spectral interferences, when narrow line sources are used, are uncommon, contrary to continuum sources. In the latter case corrections can be made by wavelength or amplitude modulation. Different wavelengths are separated from each other by filters whose advantage is their low price and good spectral transmission. Atomic fluorescence spectrometry has the simplicity, speed, cost and specificity advantages of AAS. Although at the moment AFS is essentially a single-element technique, multielement analysis can be achieved using a continuum source, a laser, sequentially tuned to different wavelengths or an ICP as light source. Few AFS instruments are commercially available such as a non-dispersive system for Hg determination (*cf.* Chapter 36) or ICP AF spectrometers.

4.6.3 X-ray fluorescence spectrometry (XRF)

Bombardment of an atom with high energy photons, electrons or photons induces removal of inner electrons (from K, L or M shells). The orbital vacancies formed are filled by outer orbital electrons giving rise to the emission of X-ray photons. The measurement of their energy (wavelength) and intensity forms the basis of XRF techniques. They are usually divided according to the design and principle of operation of the spectrometer into wavelength dispersive XRF (WDXRF), energy dispersive XRF (EDXRF) and, a modification of the latter, total reflection XRF (TXRF). Since there is a simple relationship between wavelength and energy the same basic type of information is provided and the same character of interferences encountered. There are significant differences in terms of sensitivity, selectivity, versatility, speed and price range, so that a particular technique is favoured for a given application. Various textbooks and extensive topic reviews on XRF are available [218–223]. XRF methods are usually applied to direct analysis; sample pretreatment is often required to enhance its performance. The relevant methods have been reviewed [224].

Sample

Solid homogeneous samples such as metals, glasses, ceramics or polymer disks can be analyzed directly or after polishing the surface.

Other solid specimens are ground to less than 200 mesh size to ensure homogeneity and analyzed as a loose powder, compressed powder pellet or fused glass disk. Signal intensity depends on particle shape and size, particle size distribution and packing density so these must be kept uniform. Inhomogeneity and particle size problems can be further overcome by fusion of the material, usually with Li borate fluxes, to give smooth surfaced amorphous glass disks. Despite being time consuming, the latter technique is preferred for elements lighter than iron (Na, Mg, Al and Si) whereas for elements heavier than iron it offers no distinct advantages over the pressed powders [225].

Precipitates and suspended solids can be collected on paper or membrane filters. Solutions and other liquids are evaporated on plastic films or filter papers. For TXRF an aliquot of 10–50 μl is deposited on a carrier (quartz plate) and allowed to dry. Liquids can be analyzed with no or little preparation whereas solid samples are generally decomposed prior to analysis. Finely powdered materials can be prepared as a slurry which is pipetted onto the carrier and analyzed directly. Solids can be also prepared by freeze cutting (with a microtome) into 10 μm thick sections which are placed onto a carrier and dried to be shrunk.

Wavelength dispersive XRF

The test sample is irradiated by high intensity X-rays, usually using an X-ray tube (*ca* 3 kW). The induced radiation which consists of several wavelengths is dispersed into individual spectral lines by reflection at a large single analyzer crystal (Bragg diffraction). The diffracted beams are collimated so that the diffracted radiation falls on the surface of a photon detector. Sequential WDXRF spectrometers (single-channel) contain a number of interchangeable crystals to cover the full range of measurable elements so that the composition and orientation of the analyzer crystal can be selected for optimum angular dispersion and reflectivity. A multichannel spectrometer can measure up to 28 elements simultaneously. Most of the channels can be preset for specific analyte lines.

Energy-dispersive X-ray fluorescence

In an ED spectrometer all the X-rays emitted from the sample are directed into the detector at once. The detector, an Li-drifted silicon crystal *ca* 3 mm thick and 7 mm in diameter (Si(Li)) generates a pulse of electric current having a height proportional to the energy of each X-ray photon. The detector collects emitted X-rays of all energies and

sorts them electronically. In ED instruments a smaller supply power is required (0.5 kW). The primary X-rays are filtered to minimize background and then directed on the sample. Furthermore, low-power isotopic sources can be used giving rise to low cost, transportable spectrometers [226]. Radioactive X-ray sources (^{244}Cm , ^{109}Cd or ^{241}Am for heavy elements $Z > \text{Ti}$ and ^{55}Fe for lighter elements) are used.

Total reflection X-ray fluorescence

If a collimated beam of X-rays (e.g. from an Mo or a W tube) impinges on an optically flat surface at a grazing angle of a few milliradians of arc (*ca* 5') total reflection will occur. The sample (as a thin layer) on this reflector is thus passed through by the primary and the totally reflected beam, whereby it is excited to fluorescence. The emitted radiation is detected by an Si(Li) detector, mounted directly above the sample, and resolved as an ED spectrum. As the primary tube photons are totally reflected they do not contribute to the sample background spectrum. The principles and state of the art of TXRF have been reviewed [227–234].

Calibration

A plot of X-ray intensity *vs* concentration is produced for each analyte on the basis of a series of standards. Standards must be similar to the sample in terms of physical form, analytes concentration range, matrix composition and physical characteristics (particle size and packing density). The intensity is not directly proportional to the concentration but is affected by all other elements present in the sample which are then mathematically resolved. Therefore, it is general practice to calibrate instruments against as many reference materials as possible to minimize effects of discrepancies in individual "standard" samples. Standard addition and internal standard methods require fusion and good homogenization and are seldom applied. Various compensation and mathematical correction methods have been described [235]. The need for many standards is overcome when thin films, in which the intensities of the analyte lines are directly proportional to the concentration and are matrix independent (e.g. TXRF), are analyzed. Only a single internal standard element is needed even for multielement analysis over a dynamic range of more than 3 orders of magnitude.

Detection limits and precision

The minimum detectable concentration is inversely proportional to the sensitivity and directly proportional to the square root of the

background response in counts per second at the analyte wavelength. The sensitivity is determined by the power of the source, the spectrometer efficiency for the given wavelength and the fluorescent yield of the excited wavelength. The value of the background is determined mainly by the scattering characteristics of the sample matrix (scattering of the *bremssstrahlung* from the source) and the intensity-to-wavelength distribution of the source (Compton background). The sensitivity varies by *ca* 3 orders of magnitude over the measurable element range. It decreases with the decreasing atomic number because of the decreasing fluorescence yield and increasing absorption effects with increasing wavelength of the analyte line. The most sensitive elements are generally the transition metals where direct measurements down to ppm levels (0.1 μg absolute) are possible in less than 1 min. Longer X-ray wavelengths of elements with atomic number below that of $_{40}\text{Ti}$ are strongly absorbed by air which is evacuated from modern instruments. XRF is not used for analyses of elements below $_9\text{F}$. Even in vacuum spectrometers the sensitivity diminishes below $_{12}\text{Mg}$. The least sensitive elements are those below $_{14}\text{Si}$. X-ray spectrometers are optimized for either light or heavy element analysis. This is achieved by choosing appropriate filters for EDXRF or by using a light or heavy element anode. WDXRF detection limits for the light elements are significantly lower (1–2 orders of magnitude) than ED data but for heavy elements they are comparable. Accelerator-based excitation with high energy protons (proton-induced X-ray emission, PIXE) provides increased sensitivity [236]. Total reflection XRF is superior in terms of detection power by 1–2 orders of magnitude over PIXE. Elements heavier than $_{11}\text{Na}$ can be determined with an ADL of 10–100 pg or down to 1 pg for elements around $Z = 25$. Consequently the ng g^{-1} region is reachable for solid samples (100 μg) or ng l^{-1} for solutions (100 μl). Precision of XRF techniques in trace analysis is below 5% and is governed by counting statistics and sample inhomogeneity.

Selectivity and interferences

Wavelength dispersive XRF offers high resolution and ease of the determination of the line intensities. Selectivity of EDXRF is defined by the characteristics of the Si(Li) detector which has limited energy resolution resulting in frequent peak overlap occurring. Matrix effects are serious and decrease with decreasing thickness of the sample. Variations in matrix composition affect the signal considerably. They can be alleviated by dilution methods, compensated by the use of an

internal standard, corrected mathematically or eliminated by using thin films or removal of the matrix. Dilution of the sample with an absorber, e.g. La_2O_3 or BaSO_4 , reduces the matrix differences between different samples and standards. The mass absorption coefficient of a sample is raised to a level at which variations in the absorption coefficient due to changing concentrations of matrix components are reduced. The diluent must be well mixed with a sample, e.g. by fusion. An alternative is a large dilution (1:100) with a low-absorbing diluent. Both methods, however, degrade detection characteristics.

Versatility, cost and turnover

Most commercial instruments generally cover the X-ray wavelength range between 0.2 and 20×10^{-12} m. This allows measurement of the K series from ${}^9\text{F}$ to ${}_{71}\text{Lu}$, and the L series from ${}_{25}\text{Mn}$ to ${}_{92}\text{U}$ with varying sensitivity. Conventional XRF instrumentation is based on WD spectrometers. They generally perform satisfactorily over the middle range of wavelengths but suffer from lack of resolution for shorter wavelengths (high energies) and sensitivity (net detected intensity) at longer wavelengths (low energies). Alternative dispersive elements known as layered synthetic microstructures enable analysis for very light elements down to ${}^4\text{Be}$ [221]. XRF has a wide dynamic range (ca 6 orders of magnitude) and may be used for analyses from the low ppm range to several percent. Modern instruments are capable of high speed analyses with good sensitivity to the low ppm range. For EDXRF, counting time is typically 100–10 000 s (ca 10–30 times that of WDXRF), which is offset by the ability of simultaneous multielement analysis. The time required for sample preparation is very small if loose or pressed powders are suitable as samples. Sample preparation may be the time limiting part of the total procedure.

Whereas a WD system identifies and quantifies only those elements for which it is programmed, an ED spectrometer measures all elements within its range simultaneously and thus is more useful in recognizing unexpected elements. The disadvantage is the need to maintain the Li(Ge) detector permanently at cryotemperatures and in a clean vacuum. Further, the usefulness of a conventional Si(Li) detector in the low energy range (up to 3 keV) is severely limited by the significant absorption of soft X-rays in the Be window of the cryostat. 0.5 μm thick polymer windows offer an improvement in the sensitivity to elements of low Z. Elements lighter than Na can be detected by TXRF, if ultra-thin (0.4 μm) diamond-like carbon windows are used for the detector, or

even windowless detectors and vacuum chambers [237,238]. Simultaneous WD instruments are required where the need for high throughput quantitative analysis (up to 28 elements within a few minutes) is of the essence and high cost can be justified. Sequential WD instruments are cheaper and even more accurate but at the expense of speed (*ca* 1 min for the determination of a designated element). Energy-dispersive instruments are recommended wherever initial cost is a major consideration, semiquantitative analysis can be accepted and unexpected elements can occur. Modern commercial X-ray instruments are accompanied by integrated measurement and data presentation systems. The implemented software allows for the complete control of the hardware, making fully automated and unsupervised measurements possible and computed results can be visualized immediately.

4.7 ACTIVATION SPECTROMETRY

Techniques of this group are based on the measurement of the radiation emitted by a radioactive nuclide produced when a neutron or charged particle has been captured by a stable analyte nuclide. The energy of γ -radiation emitted is nuclide characteristic and enables the identification of the target analyte whereas the intensity is the basis of quantitation. The most widely used is neutron activation analysis (NAA) with γ -ray spectrometry. Activation with charged particles, which is becoming popular for lighter elements, is beyond the scope of this book [239]. Several monographs and review papers on NAA are available [240–249].

4.7.1 Irradiation and measurement

The sample, typically 1–100 mg of solid or evaporated liquid, is irradiated in a nuclear reactor, usually for *ca* 12–14 h in a flux of thermal neutrons of *ca* 1×10^{14} n cm⁻² s⁻¹. Epithermal neutrons are enjoying increasing popularity for some applications [250]. After removal from the reactor, samples are allowed to decay (cool) to permit unwanted short-lived activity (e.g. ²⁴Na) to diminish. Typically isotopes with half-lives from several hours to several days are used for analysis. Alternatively, short-lived isotopes (with half-lives in the range from 1 min to 3 h) can be used, which requires very short irradiation times (0.5–30 min), at the expense of the need for very fast transport facilities

and data acquisition hardware and software to handle high counting rates and to process the accumulated data.

Gamma-ray spectra from activated samples (usually in the range 60–1600 keV) are measured using high purity germanium or Li-drifted Ge semiconductor detectors or NaI scintillation detectors interfaced to a computer-controlled multichannel pulse-height analyzer system for data acquisition and reduction. The radiation can be measured without any sample pretreatment (INAA) or after taking up the irradiated sample into solution and a series of separations (RNAA).

Absolute analysis requires the accurate knowledge of the nuclear reaction cross-section and the effective flux density and is practically impossible. Therefore, a comparator method is used in which standards containing known amounts of the element(s) of interest are irradiated simultaneously with the samples [251]. The calibration graph is then the straight line drawn between the activity in the calibration standard and the origin. Calculations must be corrected for difference in neutron flux between standard and sample and for radioactive decay in the course of the time between counting the sample and standard.

Calibration with synthetic multielement standards has been proposed [246,252]. The use of CRMs for this purpose is not recommended because of their scarcity and a relatively large margin of uncertainty regarding the certified values. This is of particular concern for NAA as it is the primary certification method so the same errors are likely to be magnified. Serious photopeak interferences in the standard spectrum may be present.

4.7.2 Analytical characteristics

Detection limits, precision and dynamic range

NAA offers ADLs at the microgram level for many elements and down to ng quantities for some. It is especially sensitive for the REEs and Ag, Au, Cu, Ir and Rh. The detection limit obtainable depends on many parameters, including nuclear constants, neutron flux, and counting time, but is especially constrained by the magnitude of the background continuum from the matrix which is a result of the high activity of a few isotopes (^{24}Na , ^{60}Co , ^{59}Fe , ^{45}Sc and ^{50}Cr). An improvement by a factor of 10–100 can be achieved by radiochemical separation of nuclides to be counted from the matrix activity. The procedures are multistep, tedious and time consuming and require specialized facilities for the manipulation of relatively radioactive material. Carriers are

added to minimize adsorption and other non-equilibrium effects during separation and preconcentration. Radiochemical separation procedures have been reviewed [253]. NAA has a precision of a few percent at the ng/g level unless counting statistics is a limited factor. The dynamic range is controlled by self-shielding.

Interferences and sources of error

Spectral interferences arise from the overlap of adjacent γ -peaks due to broadening and are strongly sample dependent. Exhaustive references can be found elsewhere [254]. Interferences can be overcome by choosing an alternative interference-free γ -photopeak, advanced mathematical resolution of the overlapping peaks or recounting the sample after a suitable decay period after which the interfering activity has substantially decreased. Nuclear interferences arise when the same product nucleus can be produced from different nuclides present in the sample, e.g. the case of ^{28}Al which may be produced from ^{27}Al , ^{28}Si or ^{31}P , that of ^{52}V (from ^{51}V or ^{52}Cr) or radionuclides produced *via* fission of uranium (e.g. ^{95}Zr , ^{103}Ru , ^{137}Cs , ^{140}Ba and ^{144}Ce) and products of their decay. Background radiation which results from cosmic rays and decay of naturally occurring isotopes (especially ^{40}K , ^{232}Th series, ^{226}Ra series) can interfere and requires shielding of the detector with a thick annulus of lead (free of significant radioactive impurities). Other sources of error result from sample-detector geometry and self-shielding. The exact reproducibility of the position and dimensions of the counted sample are critical. Neutron self-shielding occurs when an element in the sample matrix (e.g. B) absorbs neutrons, thus reducing the population available to activate the analyte element. The effect increases with the sample weight and can be identified by comparing signal per mass unit from different sample weights.

Versatility, cost and turnaround time

Neutron activation analysis is specific, highly sensitive and applicable to almost every element (except of some lighter elements and Pb). It can be applied to microsamples (1 mg or less) and one irradiation can provide information on 30 or more elements. The sample size can be increased to several grams with transparent matrices increasing the sensitivity. NAA is blank free and overcomes the need for expensive clean-room facilities. Access to a nuclear reactor and special protocols are required. The analysis time depends on the elements to be measured. Instrumental NAA with short-lived isotopes is particularly at-

tractive with irradiation and counting taking a few minutes. Radiochemical NAA should not be considered as the technique of choice unless the analytical results cannot be obtained by other means. The cost of INAA is competitive with those of other techniques which provide an equivalent range of elements and DLs. Instrumental NAA is of particular interest to forensic studies, paint and glass analysis. It has been widely applied to the analysis of a variety of samples including geological, biological, environmental and industrial materials (*cf.* Part II). Radiochemical NAA on the other hand has been playing an important role in the certification of reference materials at the ppm and ppb levels [255].

4.8 MASS SPECTROMETRIC TECHNIQUES

These are based on the measurement (counting) of ions produced in a high temperature environment. Ions are identified on the basis of the mass-to-charge ratio which is characteristic of a given isotope. The dependence between the number of ions and the concentration of a given isotope in the sample is the basis of quantification. The components of a typical mass spectrometer include an ion source, mass analyzer for dispersing ions according to their mass-to-charge ratio, and an ion detector and read-out system. Mass spectrometric techniques are usually divided according to ion source. Plasma source MS which enjoys the largest popularity is discussed in detail below but each of other sources often offers unmatched characteristics for specific applications [256].

Features common to MS techniques include the possibility of isotope-specific analysis and the generally very low background count rate leading to low detection limits. Mass spectrometric techniques are plagued (to differing degrees) by isobaric interferences (molecular and multiply charged ion species having the same nominal mass-to-charge ratio as the isotope of interest) which are matrix dependent and degrade sensitivity, precision and accuracy. The state of the art of inorganic MS techniques has been reviewed [256–258].

4.8.1 Inductively coupled plasma mass spectrometry

An ICP argon plasma (*cf.* Section 4.5.3) is used as the ion source. Plasma gases are extracted through an orifice into a chamber held at 1 torr and then passed into a mass analyzer for dispersion and measurement.

The rapid increase in the interest has been reflected in a number of books and review papers covering various aspects of ICP MS [259–273].

Instrumentation

An ICP mass spectrometer is composed of (1) a sample introduction system, (2) an argon plasma torch configured at 90° with respect to conventional ICP AES operation, thus allowing plasma gases to be sampled through an orifice, *via* a differential pumping unit into the quadrupole mass filter and (3) a quadrupole mass spectrometer and associated data collection electronics which permit rapid scanning of selected mass ranges between 0 and 300 daltons. The whole system can operate unattended if equipped with an autosampler; it is currently available from several manufacturers at a price of *ca* \$200,000–300,000. Atomization source may be placed in a glove box for radioactive materials analysis [274]. The sample is usually taken up in solution and introduced into the plasma *via* a pneumatic nebulizer and a conventional spray chamber. The salt load is limited to *ca* 0.2–1% by sampling orifice clogging. Alternative methods, slurry sampling, ETV, FI processing and laser ablation, are enjoying increasing interest (*cf.* Section 4.2).

Data acquisition

The basic optimization criterion is maximizing the total ion signal. The effects of operating variables including flow rates of argon to the torch, forward power delivered to the plasma, observation height and sample uptake rate have been discussed [275–277]. The mass spectrum is built up by single-ion monitoring (SIM), peak hopping over the specified isotopes or repeatedly scanning over the required mass range. The SIM mode is seldom used but, if only one element needs to be determined and an overlap-free peak is available, offers the best performance in terms of sensitivity. In the peak hopping mode the quadrupole voltages are jumped to transmit specific mass-to-charge values. Hence, only data for peaks of interest are acquired and, as no time is wasted in blank regions of the spectrum, a larger proportion of the analysis time can be spent on the smallest peaks, thus improving their counting statistics and detection limits. The data are collected at the centre of the peak which, on the one hand, improves sensitivity and abundance sensitivity but, on the other hand, adversely affects the precision owing to the imprecision of centring. The scanning mode involves scanning a spectral region at a uniform rate collecting data in a multichannel analyzer operated in the multiscaling, i.e. time-based, mode. A number of scans

are summed and treated as a single spectrum. This approach records the shape of the peaks in the mass axis. The intrinsic inability to skip non-interesting mass regions, however, makes the measurement slower and less sensitive. A continuous signal is needed for the scan duration unless a rapid scan facility is available on the instrument.

Calibration

Quantitation is done either by measurement of the peak height count rate at the peak apex or as integrated peak area. The instrument and solvent background response is subtracted from the sample response. The calibration curve is reliable for simple matrices but a standard addition technique needs to be applied for more complex samples. The large dynamic range and multielement capability favour internal standard calibration. The possibility of isotopic ratio data acquisition enables isotope dilution techniques where high accuracy is essential for non-monoisotopic elements (*cf.* Ref [278]). On the contrary, rapid semiquantitative analysis using programs invoking a pre-established response is possible with a moderate accuracy (*ca* 30%) at low ppm levels [279].

Detection limits, precision, dynamic range

ICP MS is a very sensitive technique which is reflected in the DL values summarized in Fig. 4.4. Sensitivity is fairly uniform (within a factor of 3) for the majority of elements with first ionization energies below 10 eV. The instrumental DL for a given isotope is inversely proportional to the integration period for its signal and thus dependent on the acquisition mode. They are virtually equal for the SIM and peak-hopping modes provided that integration times for a given peak are equal in both cases. In the scanning mode a 1 min integration over 240 daltons reduces the effective integrating time for each isotope to about 0.25 s, i.e. an order of magnitude less than for SIM, which is followed by the deterioration of the sensitivity to a similar degree. Detection limits can be improved by the use of a high resolution mass spectrometer which considerably (by *ca* 2 orders of magnitude) reduces the background count rate. The largest gains are observed where the DLs in conventional MS are affected by polyatomic interferences [280–283]. The experimental DLs depend on the efficiency of sample introduction and signal suppression effects during ionization and ion counting. A precision of 1–3% at the pg/ml level is usually obtained. It is limited by drifts in sensitivity, instrumental noise and counting statistics. The dynamic range reaches 6 orders of magnitude.

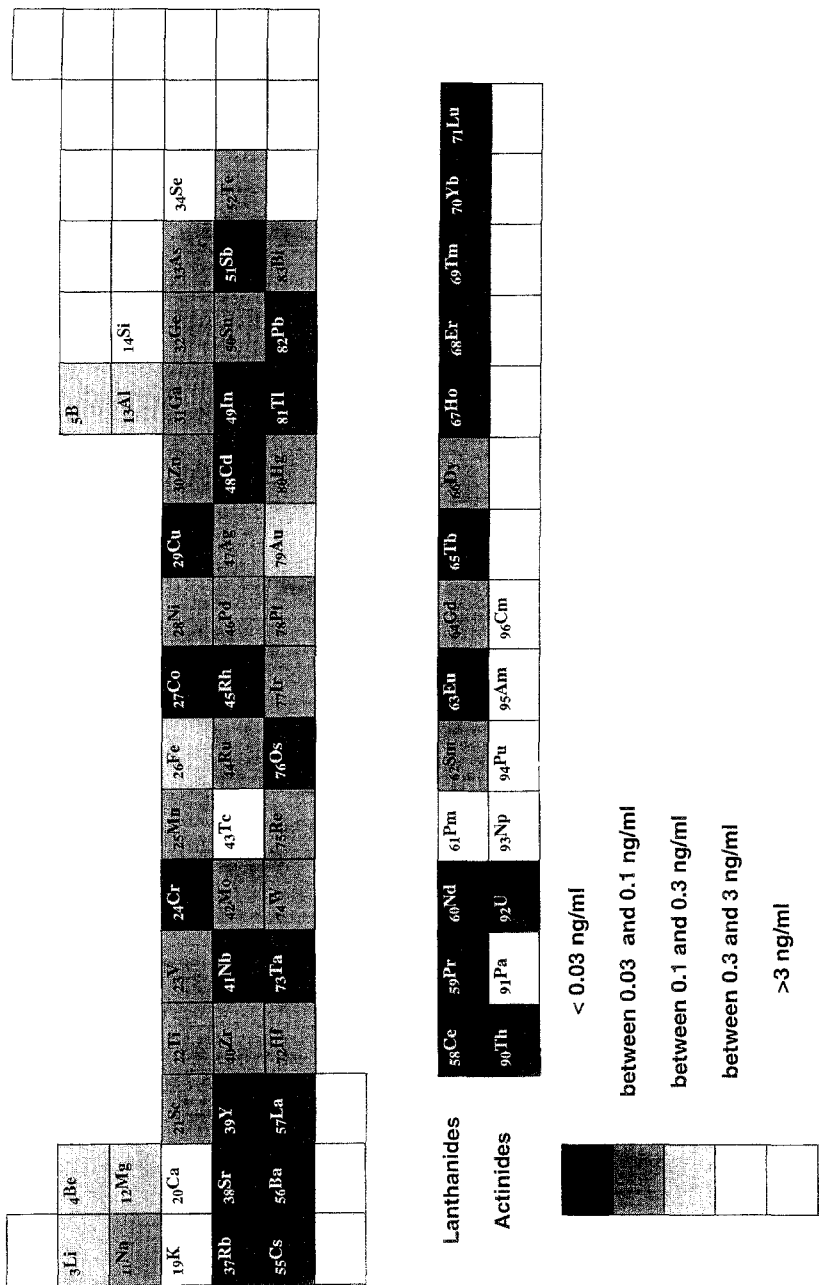


Fig. 4.4. Detection limits in ICP MS.

Selectivity and interferences

Selectivity in ICP MS is usually considered in terms of so-called abundance sensitivity which is a measure of the ability to detect an ion at a mass-to-charge ratio adjacent to that of an ion present at a high concentration. It is defined as the ratio of the intensity of the tail of the major peak (at the mass of the minor isotope) relative to the intensity of the major peak itself. Typical values of abundance sensitivity are 10^{-6} .

Non-spectral interferences are similar to those of ICP AES in terms of irreproducible nebulization and atomization in the plasma. Some interference effects characteristic of ICP MS include solid deposition on the sampling apertures which leads to clogging the orifices and suppression of analyte signal, and matrix-induced suppression in the ion beam. In the latter case the degree of suppression increases with the mass of the matrix element and for the same matrices decreases for heavier elements. The differences in sample(s) and standard physical properties affecting the transport can be corrected by matrix matching in terms of solvent, salt content and acid content, standard addition (external or internal) or isotope dilution. These approaches also correct for the changes in the temperature (and hence ionization characteristics) of the plasma induced by organic solvents and excess of easily ionized elements (*cf.* Section 4.5.3). Flow injection is widely used to handle high salt content matrices [284–287].

Spectral interferences due to the overlap of the analyte lines with lines of other ions originate from the plasma gases, solvent, matrix or even other trace elements. Background mass interferences arise from the argon plasma gas (Ar^+ , Ar^{2+}), the solvent, usually water (H_3O^+ , OH^+ , ArH^+), air entrained in the plasma and impurity gases in the argon itself (N^+ , O_2^+ , ArH^+ , ArO^+ , NO_2^+ and material eroded off the aperture/skimmer assembly (Cu, Ni and Mo). They are especially important for lighter elements, e.g. ^{40}Ca is overlapped by ^{40}Ar , which makes their determination difficult. Furthermore, the acids used for either sample decomposition or stabilization of the solution fed contain N, Cl, P, S (in the increasing order of seriousness) which may combine with O, H and Ar forming a plethora of mixed ions. The problem of polyatomic ions has been dealt with in detail in several publications [259,261,276,288–291]. Interferences of this type are removed by changing the plasma gases or solvent [292–297], or alternative sample introduction techniques such as ETV or LA (*cf.* Section 4.2.2), or cryogenic desolvation [298,299]. The high temperature of the plasma makes the ICP MS spectrum relatively simple compared with that of other MS techniques. Interelement inter-

ferences can be predicted with confidence (only 211 mass lines in total for all the elements). They are usually easily overcome as all elements except In have at least one line free of overlap. Commercial instruments take into account the isotopic abundances in their software and the operator is alerted to any potential interferences when setting his run procedures [300]. Oxide ions can be formed in the plasma typically with 0.01–0.1% efficiency. Such low levels can cause an interference if an element in question is present as a major component in the matrix. Determination of ions 16 daltons higher may be difficult if there are no other isotopes to use for the measurement. A similar type of interference results for doubly charged ions of a major matrix element. Because ions are filtered in the mass analyzer on the basis of mass-to-charge ratio m/z , doubly charged ions appear in the spectrum half the mass of the parent singly charged ion. Oxide, double charged and dimer interferences have been discussed [301–303]. Spectral interferences are considerably alleviated with HR ICP MS which enables the masses of polyatomic ions to be determined very accurately and thus their unambiguous identification [280–283]. Interferences in ICP MS have been comprehensively reviewed [304].

Isotopic analysis

ICP MS has an intrinsic ability to determine individual isotope ratios which makes it suitable for stable isotope tracer studies and in isotope dilution quantification for selected elements. Quantification can then be done from one spectrum taken in the peak hopping or scanning mode. Accurate measurements of isotope ratios will be limited by overlapping of adjacent peaks, especially in the case of minor isotopes adjacent to major isotopes [305,306]. As resolution is increased, transmission and thereby sensitivity are decreased. If counting statistics is not limiting, isotope ratios can be measured with a precision of 0.1–1% for a broad range of stable isotopes [307]. This cannot match the precision of TI MS with a magnetic sector but is sufficient for many applications. Linearity of the isotopic ratio over a decade is observed. The applications include biomedicine, geochronology, studying the mixing of oceans and magmatic bodies, determining palaeo- and magmatic temperatures, sedimentation rates and identification of origin sources.

Versatility, cost and turnover

ICP MS is a highly versatile technique. It is especially suitable for heavier metals and is able to determine essentially all the isotopes

including halogens (as negative ions [308,309]) in a variety of samples. For Ti, V, Cr, Mn, Co, Ni, Sn and W very clean blanks, reagents and equipment are required. The ICP MS technique combines the freedom from matrix interferences characteristic of the ICP with the very favourable signal-to-background ratios obtainable by MS. Simultaneous analysis down to ng/l level (solutions) or ppm level (on a solid sample basis) is possible at preset instrument conditions. Sample preparation is minimal except in cases of isobaric overlaps. The analysis is rapid; with the conventional nebulization introduction *ca* 50–100 samples can be processed per day. This can be increased and the analysis run unattended by using flow injection sample introduction. The drawback of ICP MS is a high investment cost (\$200,000–300,000) and relatively high running costs which, however, are similar to those of the widely used XRF techniques. It is indispensable in commercial and industrial laboratories where a high investment cost is justified by the large number of samples analyzed.

4.8.2 Other mass spectrometry techniques

Thermal ionization mass spectrometry

A sample is loaded onto an Ta or an Re filament and ionized by electrically heating the filament to a controlled temperature. Ions are extracted into a mass analyzer by applying an electrical field. A simple magnetic sector analyzer is usually used for mass dispersion but instrumentation is expensive. Quadrupole mass analyzers eliminate this drawback at the expense of slightly reduced precision. The technique is particularly suited to metals with low ionization energy producing positive ions and non-metals with high electron affinity producing negative ions. The metals which yield low ion beam currents include As, B, Se, Si, Te, Au and PGM, and some refractory metals (W, Os). The sample must be in a suitable chemical form to ensure a stable ion beam during the analysis. Isobaric interferences are persistent and chemical isolation of the analyte element is essential. The accuracy is seldom limited by the measurement but by inhomogeneity and blank problems. Despite the evident disadvantages such as long measurement time (in extreme cases several hours) and the need for tedious, contamination-prone and time-consuming sample preparation, TIMS remains unmatched for precise determination of the relative isotopic abundances in geochronometry and for highly accurate isotope dilution measurements (*cf.* Section 4.9.4). Applications of TIMS have been reviewed [310–315].

Microwave-induced plasma mass spectrometry

Trace analysis in high matrix aqueous solutions using helium MIP MS has been discussed [316]. High sensitivity MIP MS for trace element analysis was developed using a surfatron cavity [317]. Microwave-induced plasma MS is a suitable technique to be used as a GC detector [318].

Spark source mass spectrometry

A sample is mixed with an electrically conducting binder and compressed to form an electrode. Ions produced as a result of an RF electrical discharge between the sample electrode and a counter electrode are sampled to a mass analyzer, usually magnetic sector doubly focusing. The technique is applicable to solids and allows the entire mass spectrum to be obtained with a good detection limit (sub-ppm) and excellent resolution. It is plagued by considerable isobaric interferences and large fluctuations of the ion beam. The instrumentation is expensive and must be handled by an experienced operator. The technique was reviewed in 1984 and is slowly coming out of use [319].

Electron impact ionization mass spectrometry

The ion source is an electron impact source. A single magnetic sector or quadrupole analyzer but ion trap is used. Instruments are designed with double or triple collection of the ion beam, permitting simultaneous detection of isotope ratios of interest. Electron impact MS is used as detector in GC for speciation of organometallic species.

Glow-discharge mass spectrometry

GDMS is used for the analysis of solid, usually non-conducting and semiconducting, materials. The sample is atomized by cathodic sputtering and ionized by a glow discharge in a working gas (usually argon) at reduced pressure. Ions are sorted according to mass by a quadrupole filter (low resolution) or a double-focusing device (high resolution). Isobaric interferences from residual gas species and dimers of the analyte and calibration problems are common. Detection limits in the low ng/g region and even below can easily be reached. Precision of a few percent is common and the dynamic range reaches *ca* 9 orders of magnitude. Reference materials are required for calibration but semi-quantitative analysis in the ultratrace region is possible, making the technique attractive for ultrapure metals and semiconductors. Glow discharge MS has been reviewed [320–323].

Laser-induced mass spectrometry

This involves ion production by the interaction of an energetic laser pulse. They are mainly used for microscopic analysis and based on time-of-flight (TOF) mass analyzers. Several laser microprobe mass spectrometers are commercially available [324,325].

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Quantification techniques

5.1 CALIBRATION GRAPH

The calibration graph is established by plotting the signal intensity for a set of standards against the concentration. In the most common case this is a straight line: $y = a + bx$ where a denotes the blank value of the analytical procedure and b the sensitivity of the analytical method. The coefficients a and b are calculated according to the least squares fit procedure [1]. Non-linear graphs have become popular since the advent of microprocessors [2]. Modern spectrometers are sold with a software package which can determine the calibration function automatically and present the analytical data in desired units.

Quantification using a calibration graph is an interpolation method which means that the readings of all the sample solutions must lie between the lowest and highest readings of the standard solutions. For the highest accuracy, standards are measured before and after sample solutions. For large sets of samples standards are measured at regular intervals. The blank is usually measured between the standards and samples to ensure the stability of the base line. The signal from the sample is directly compared with a set of standard solutions. The calibration graph method is unable to correct for either additive interferences (blank, spectral signal enhancement) or multiplicative interferences (matrix suppression or enhancement) unless matrix-matched standards are used.

5.2 THE METHOD OF STANDARD ADDITIONS

The method of standard additions (MSA) involves the spiking of at least one aliquot (usually two or three) of the test sample with known

concentrations of the analyte. The original sample and the spiked samples are then analyzed to produce signals to establish a standard addition curve which is the basis for the calculation of the analyte content. For solid samples the spikes should be added before any chemical treatment and sufficient time for its interaction with the sample matrix should be given.

The MSA does not correct for additive interferences (blank, spectral overlaps) but usually does correct for matrix-related suppression or enhancement effects. It can be applied only provided that (1) signals measured from the original and spiked samples fall within the rectilinear range of the calibration curve and (2) the sensitivity of the method is not changed by spiking. The MSA is an extrapolation method and usually its accuracy is not as good as that of an interpolation method. The technique is fairly time consuming (the analysis time is usually tripled). It is essential that the spike is exactly the same species as that actually present in the sample or, at least, that the present and the spiked species become identical on a chemical treatment of the test sample.

5.3 INTERNAL STANDARDIZATION

An internal standard (IS) is an element (either absent in the sample or present at a constant level) which is added to all samples (if not already present), standards and blanks. The ratio of the signals of the analyte line and an internal standard line is measured. The instrumental response (y_A) of the analyte concentration (x_A) is thus corrected for the response of the internal standard (y_{IS}). In practice a calibration graph $y_A/y_{IS} = a + bx_A$ is constructed where a denotes the blank and b the sensitivity of the method. In the simplest case (no blank, one-point calibration):

$$x_A = \frac{y_A y_{IS_{ST}}}{y_{IS_A} y_{ST}} x_{ST}$$

where x_A and x_{ST} denote concentrations, y_A and y_{ST} signal intensities at the analyte line and y_{IS_A} and $y_{IS_{ST}}$ signal intensities at the internal standard line for the test sample (A) and calibration standard (ST).

The internal standard method is usually used to correct for fluctuations in experimental conditions (amount of sample analyzed, nebulizer

and source performance) and to improve the precision. In many cases matrix effects can be corrected for as well. The method requires that the IS (1) responds similarly to the analyte to the interferences it is expected to correct for, (2) does not interact with the analyte or sample matrix and (3) can be determined in the same run as the analyte (EDXRF, ICP MS, simultaneous ICP AES). Under the above caveats, it is convenient to use the major matrix element as the IS provided that the analytical techniques have a wide dynamic range.

5.4 ISOTOPE DILUTION ANALYSIS

The technique can be applied only to the elements which possess more than one naturally occurring stable isotopes. Monoisotopic elements can only be analyzed if there exists a suitable radioactive isotope having a long half-life, e.g. Th. Analysis of elements with two naturally occurring isotopes, one of which has a natural abundance of less than 1%, is subject to additional errors. If measured isotope ratios are to be corrected for mass fractionation, the element must possess three or more naturally occurring isotopes, two of which are present in the analyzed sample at a natural or known isotopic abundance.

A known weight of sample is spiked with a known amount of the analyte enriched in one of the isotopes. On equilibration the ratio between the spiked mass peak and an unspiked, naturally occurring isotope is determined. The result, together with the isotopic abundance of the enriched spike and the known natural isotopic abundance of the analyte element is the basis of quantification. The theory of isotope dilution quantification has been summarized [3,4] and can be found in virtually any monograph on mass spectrometry.

Isotope dilution is able to correct for all kinds of interferences throughout the whole procedure except for additive interferences (blanks, signal enhancement due to overlaps). The separation of the analyte element which is mandatory in some techniques (TI MS, GC-MS) and recommended in others (ICP MS) does not have to be quantitative. On the other hand, in order to minimize errors the amount of spike added to the sample must be carefully controlled.

Although considered to be an accurate method some errors may occur which include: (1) inhomogeneity errors in some sample types, due to a small mass usually taken for analysis, (2) non-equilibration between sample solution and spike due to either incomplete dissolution or

kinetic stability, (3) errors in sample and spike weightings and (4) uncertainties in mass fractionation correction. A disadvantage is the need for enriched spikes which are not available for all elements and tend to be expensive.

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Speciation analysis

Speciation of trace elements has become an important and challenging issue during the past decade because of its impact on some key disciplines including environmental chemistry, toxicology, clinical chemistry and energy-related industry [1–7]. The term “speciation” denotes, according to the IUPAC definition, the process yielding evidence of the atomic or molecular form of an analyte, so it is usually interpreted to refer to qualitative analysis only. In order to define the process of quantitative determination of trace element compounds the word “analysis” is added. Trace metal speciation analysis refers to the ability to define which forms of a given element appear in a particular sample and at what levels precisely these species occur. Note that the meaning of the word “element” in the context of speciation analysis is restricted to metals and metalloids in order to avoid the connotation: “speciation of carbon” instead of “organic analysis”. The species of interest can be divided into three basic groups as depicted in Table 6.1.

TABLE 6.1

Species of interest in trace speciation analysis

Redox systems	Alkylelement	High molecular mass compounds
Se(IV)/Se(VI)	Methyl- Hg, Ge, Sn, Pb, As, Sb, Se	Metalloporphyrines
As(III)/As(V)	Ethyl- Pb, Hg	Metalloproteins
Sb(III)/Sb(V)	Butyl- Sn	Metallo drugs
Cr(III)/Cr(VI)	Cyclohexyl- Sn	Metalloenzymes
Fe(II)/Fe(III)	Octyl-Sn	Arsenosugars

6.1 INSTRUMENTAL APPROACHES

A valid procedure must be able to discriminate among the different chemical forms of the same element, both organic and inorganic. Many operationally defined approaches have been presented [1,2]. The universally accepted approach to speciation analysis is offered by hyphenated techniques (tandem, coupled, hybrid) [8] which are based on an *on-line* combination of chromatographic separation with a sensitive and species-selective spectrometric detection. The separation and determination techniques were discussed in Chapters 3 and 4, respectively whereas below the interface-specific issues related to speciation analysis are discussed. Gas chromatography is favoured because of the absence of condensed mobile phase resulting in no need for nebulization and a low background contribution in the detector itself. The principal disadvantage of GC is the need for derivatization of analytes prior to analysis as the native species are usually ionic and lack the necessary volatility and thermal stability. Element-specific detection in gas chromatography has been reviewed [9–12]. Liquid chromatography eliminates the need for derivatization but suffers from the lack of sensitive detectors. Nevertheless, the explosive development of ICP MS has stimulated advanced speciation analysis with HPLC [13,14]. Supercritical fluid chromatography is still in its infancy in speciation analysis [13].

6.1.1 Gas chromatography–atomic absorption spectrometry

The interfacing is fairly easy. For FAAS, the GC effluent passes *via* a short piece of heated tubing (acting as a transfer line) directly into the nebulization chamber or to the burner itself. The low sensitivity resulting from the short residence time of the atoms in the flame, the dilution by the combustion gases and low flame temperature can be avoided by using ceramic tube atom traps which are heated in the flame and are positioned in the light beam. An alternative atomization cell is an electrothermally heated silica tube. In the simplest arrangement, the chromatographic column is contained in the long arm of the T-furnace and the effluent then passes into the cross-piece atomizer purged with hydrogen and nitrogen (air) gases. The evolution of the GC–AAS coupling from flame to electrothermal QF–AAS has been discussed [12]. Theoretical considerations for the development of a quartz furnace atomizer have been reported [15]. Graphite furnace AAS as a detection technique requires a specific approach regarding the connection of the

GC column to the graphite furnace. There are two principal methods for introducing the GC effluent into a GF atomizer. One of them consists in forcing the sample gas to enter the graphite furnace at the inner gas flow entrance and to follow the flow path that would normally be taken by the purge gas inside the furnace and, in fact, to replace the purge gas flow. The GC effluent follows a symmetrical path from both ends of the tube and exits through the normal sample introduction hole. This method, although very simple and elegant, fails for less volatile compounds because of condensation problems at the cooling parts of the graphite furnace. An alternative way of interfacing is enlarging the sample port of a conventional graphite tube to fit the GC column and to let the column effluent impinge directly onto the heated graphite furnace. This design works successfully for less volatile species.

6.1.2 Gas chromatography-atomic emission spectrometry

In a flame photometric detector (FPD), GC effluent is mixed with air (oxygen) and then introduced into a hydrogen flame. The FPD was initially developed for the detection of nitrogen, phosphorus and sulphur but it turned out to be an excellent detector for organotin compounds owing to its wide availability, low cost and competitive performance [16]. Plasma AES is more versatile owing to increased sensitivity and a larger number of elements which can be efficiently determined [14]. The atmospheric pressure helium MIP (*cf.* Section 4.5.5) is the most popular owing to more sensitive detection especially of non-metals, high elemental selectivity, versatility as a result of easy tuning to a given wavelength, the possibility of simultaneous multielement analysis and a wide dynamic range (4–5 decades) [17,18]. A commercial GC–MIP AE spectrometer is available [19,20].

6.1.3 Gas chromatography-mass spectrometry

The high sensitivity, together with the commercial availability of instrumentation for MS of molecular ions and a lot of expertise coming from organic analysis makes GC–MS an attractive technique of not fully realized potential in speciation analysis. Some additional features include the possibilities of confirmation of the analyte identity and standards purity control. Coupling GC to ICP MS or MIP MS is easily accomplished by connecting the column to the inner tube of the torch using a transfer line between the GC oven and the plasma torch [21].

The transfer line usually consists of a piece of metal tubing that houses either the analytical column or a piece of deactivated fused silica capillary. Applications of plasma MS in speciation analysis have been reviewed [13].

6.1.4 Liquid chromatography–mass spectrometry

The major requirement for interfacing LC with ICP MS is a transfer line that connects the outlet of the LC column with the liquid flow inlet of the nebulizer. The shortest possible narrow-bore tubing minimizes peak broadening resulting from the transfer line. Typical LC flow rates $0.5\text{--}2\text{ ml min}^{-1}$, are within the range usually required for pneumatic nebulization. The limitation is the low (1–5%) transfer efficiency. Direct injection nebulizers are a remedy (*cf.* Section 4.2). LC mobile phases consist typically of some combination of organic solvents, salts of buffer solutions and/or ion-pair reagents. Organic solvents influence negatively the plasma performance adversely because of increasing instability of the plasma (up to extinction in extreme cases) and deposition of carbon on the sampling cone and torch. The use of a water-cooled spray chamber and an increase in RF power (to 1.7 kW) can help to reduce the solvent load to the plasma and to increase stability. The addition of oxygen (1–3%) to the nebulizer gas flow can help to minimize carbon deposition and clogging of the sample cone at the expense of the cone's lifetime [22]. Salts can cause short-term signal depression or enhancement and cause blockage of the nebulizer and the sampling cone. Concentrations of more than 0.2% of solids and organic solvents must be avoided. The use of MIP MS as an HPLC detector suffers from the low tolerance of MIP to liquid samples [23]. Potential of LC ICP MS for trace metal speciation has been discussed [24].

6.1.5 Supercritical fluid chromatography–mass spectrometry

In SFC the separation is performed with the mobile phase in the supercritical state (*cf.* Section 3.5.3) whereas for the detection the supercritical fluid is decompressed to a gas. The supercritical conditions in the column are maintained by a restrictor (a piece of fused silica tubing) at its end. The interfacing to ICP or MIP MS is similar to that in GC. The heated transfer line and heated make-up gas maintain the proper restrictor temperature. Several organoelement species were investigated but applications to real samples (e.g. petroleum) were rare.

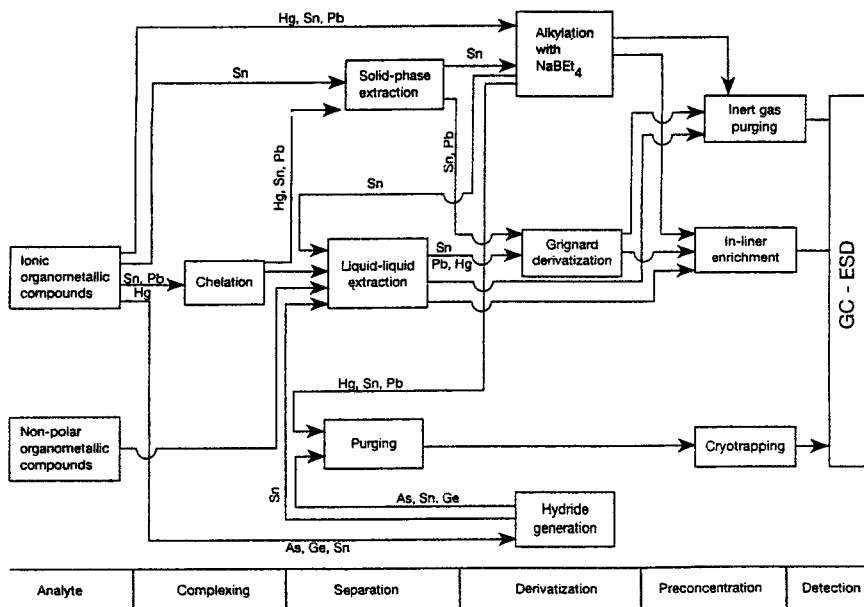


Fig. 6.1. Sample preparation for speciation analysis by GC-based hyphenated techniques.

6.2 SAMPLE PREPARATION FOR SPECIATION ANALYSIS

To be fully exploited in real sample analysis, the high instrumental sensitivity and selectivity of a hyphenated technique needs to be completed by an effective sample preparation procedure. Before chromatography analytes must be separated from the sample matrix (water, sediment, biological tissue), preconcentrated and converted to a form amenable to chromatography (derivatization in GC). Only some energy-related samples (shale oil, petroleum, gasoline) containing low polar analytes can be analyzed directly, usually after dilution.

A schematic layout of sample preparation methods used for GC-based hyphenated techniques is shown in Fig. 6.1 [12]. These methods fall into two basic categories: those based on *in situ* derivatization of the analytes followed by purging and cryotrapping and those based on the extraction (solid phase or liquid-liquid) of the analyte species, native, or as non-polar complexes (with DDTC, dithizone or tropolone), or derivatized beforehand in the aqueous phase. Liquid chromatography

based techniques need the separation of the analytes from the matrix. Specific approaches to speciation of particular elements are discussed in Part III.

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Flow-injection analysis

Flow-injection analysis is based on the injection of a liquid sample into a continuously flowing liquid carrier stream where it is usually made to react to give reaction products to be detected. FIA offers a possibility of sample handling in an *on-line* manifold in terms of separation, preconcentration, masking and colour reaction and even microwave dissolution which can be readily automated. The most common FIA advantages include reduced manpower cost of laboratory operations, increased sample throughput, improved precision of the results obtained, reduced sample volume necessary and elimination of many interferences. The fully automated FI analyzers are based on the spectrophotometric detection but are readily adapted as sample preparation units for atomic spectrometric techniques. Flow injection as a sample introduction technique was discussed in Section 4.2 whereas here its full potential is briefly surveyed. Apart from a few books on FIA [1–5], several critical reviews of FIA methods for FAAS [6–10], GF AAS [11] and ICP AES [8,11,12] methods have been presented.

7.1 GENERAL PURPOSE FI MANIFOLD

A typical FIA system consists of (1) a propelling unit, usually a peristaltic pump, which produces a flow of one or several solutions (streams), either containing a dissolved reagent or merely acting as the carrier, (2) an injection system whose function is a reproducible introduction of an accurately measured sample volume into the flow without stopping it and (3) a mixing (reaction) unit. A flow cell is required for photometric detection.

The injection volume must be changeable at least in the range 30–200 μl . Once chosen it must remain constant. The volume actually

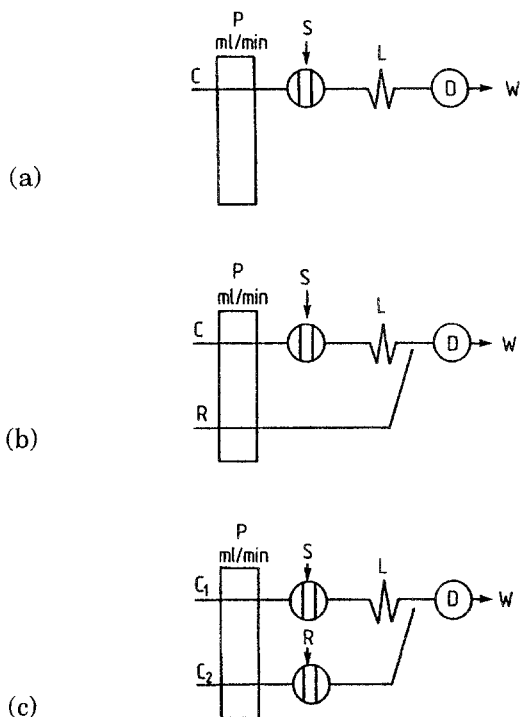


Fig. 7.1. General purpose flow injection manifolds. (a) On-line system (reagent = carrier); (b) two-line system (reagent and carrier streams separated); (c) merging zones. S: sample; C: carrier stream; R: reagent; L: mixing coil; D: detector; W: waste.

needed to fill the loop is larger. The loop is filled by aspiration and then is inserted into a carrier stream usually by means of a six-port valve. The simplest FI arrangement is the single-line configuration which is shown in Fig. 7.1(a). It can be used for rapid presentation of the sample to the detector. By suitable choices of volume injected and tube dimensions (length and internal diameter) appropriate dilution of the sample may be achieved. The carrier stream may contain a reagent: a colour-forming agent for spectrophotometry or a matrix modifier for AAS. The injected sample may also be mixed with an organic solvent to improve the nebulization efficiency. Alternatively, the sample can be injected into a carrier stream which is then mixed with a reagent stream (Fig. 7.1(b)). Both configurations have the disadvantage of a fairly large reagent consumption. The latter can be considerably diminished by

using the merging zone method (Fig. 7.1(c)) in which both reagent and sample are injected into two separate streams which are mixed at the downstream confluence point.

Some additional customized units can be introduced, usually for *on-line* separation–preconcentration, and these have been comprehensively discussed [13–15]. The automatization of this basic FIA system requires a sample-withdrawing system and an electronically controlled injection system working in coordination with the sampler.

7.2 LIQUID–LIQUID EXTRACTION

A typical extraction manifold is shown in Fig. 7.2. The sample is injected in an aqueous carrier which is segmented with organic solvent. Extraction takes place in a mixing coil. Thereafter phase separation takes place in a membrane phase separator based on the permeability of the organic phase through a Teflon membrane. A fraction of the organic phase is led through a flow cell. The back extraction mode is sometimes used. The fundamentals [16–20] and applications [15,21–23] of liquid–liquid extraction for FIA have been discussed. Virtually all FI extraction systems suffer from the gradual decrease of the hydrophobicity of a membrane and thus leakage of the aqueous phase when run on a long-term basis. A double-membrane phase separator can be a remedy [24]. Preconcentration factors achieved in FIA (usually 2–5) are considerably smaller than in batch extraction so FI extraction is used rather for the removal of matrix interferences.

7.3 LIQUID–GAS EXTRACTION

The typical applications optimized for commercial development are mercury vapour and hydride generation for atomic spectroscopy as shown in Fig. 7.3 [25,26]. The merging zone technique is usually used to inject the sample and the NaBH_4 (hydride generation) or SnCl_2 (cold vapour generation) reductant. The volatile species are generated in the reaction coil and forwarded to a gas–liquid separator. The gas phase is transported by a carrier gas (or the excess of the released hydrogen) to the detector. In comparison with the batch methods interferences from transition metals are restricted owing to the short contact time of the sample with the reagent, thus minimizing adsorption effects.

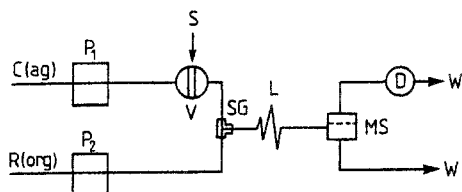


Fig. 7.2. Liquid-liquid extraction manifold. P_1, P_2 : peristaltic pumps; C: carrier stream (aqueous phase); R: reagent stream (organic phase); S: sample; V: injection valve; SG: segmentor; L: mixing coil; MS: membrane phase separator; D: detector; W: waste.

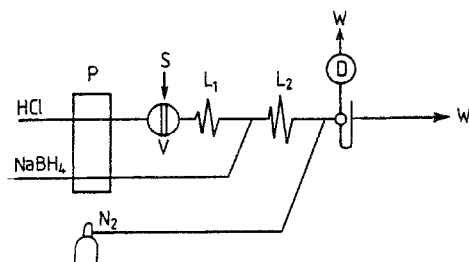


Fig. 7.3. Hydride or cold-vapour generation manifold. P: peristaltic pump; S: sample; V: injection valve; L_1, L_2 : mixing coils; D: detector; W: waste.

7.4 SORPTION

The typical manifold includes a sorption microcolumn which is operated in consecutive adsorption and desorption modes (Fig. 7.4) [27]. In the former the analytes, either native or chelated by mixing sample and reagent streams just beforehand in a flow system, are adsorbed on the microcolumn. In the desorption mode the carrier stream is changed to elute the sorbed compounds with a small volume of concentrated acid or organic solvent, usually methanol, which are then transferred to the detector. The commercially available system favours microcolumns (15 mm^3) packed with C_{18} -bonded silica [28] but other sorbents, e.g. chelating resins (*cf.* Section 3.4.3) can be used. In this way the detection limits can be improved by 1 or 2 orders of magnitude. Samples are usually introduced either by injection of a discrete volume, using an adequate sample loop, or by continuous aspiration. In the latter case knowledge

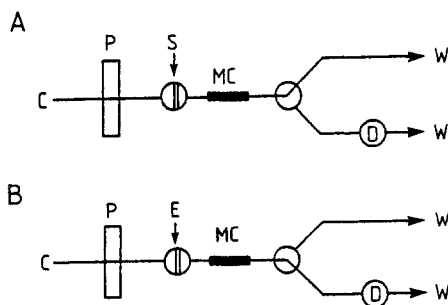


Fig. 7.4. Sorption in FIA. (a) Sorption step; (b) elution (desorption) step. C: carrier stream; P: peristaltic pump; S: sample; E: eluent; MC: microcolumn; D: detector; W: waste.

of the exact flow rate is essential but the sample is not dispersed in the carrier stream. Sorption methods have been reviewed [29].

7.5 PRECIPITATION

A sample is injected into the reagent stream (or the reagent is injected into the sample stream) to form a sparingly soluble compound which is separated from the supernatant solution on a stainless steel filter. In the simplest configuration the supernatant solution is passed to the detector and a negative signal proportional to the precipitated analyte amount is measured. In another mode the precipitate containing the analyte is dissolved by another stream and the solution formed is forwarded to the detector to produce a positive peak. The concept and applications, usually to the indirect analysis of non-metallic anions have been reviewed [30].

7.6 MICROWAVE DIGESTION

A coiled Teflon tube integrated in an FI manifold serves both as a sample container and as the digestion vessel. After a sample (injected as a slurry into an acid stream) has entered the reaction coil, the flow is stopped, the coiled tube is sealed by closing input and output valves and microwave power is applied for digestion of the sample. The concept proposed by Burguera et al. [31] was applied successfully to the analysis

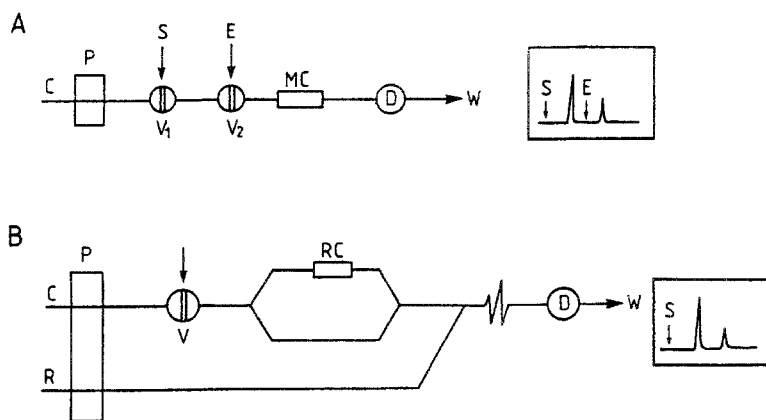


Fig. 7.5. Speciation in FIA. (a) With a column selective for one species; (b) with sample splitting. C: carrier stream; P: peristaltic pump; V: injection valve; S: sample; E: eluent; MC: microcolumn; RC: reduction (oxidation) column; D: detector; W: waste.

of biological samples [32–34]. The shortcomings of the system stem from the use of fairly large volumes of acids and from delays arising during cooling of the digests and cleaning of the tube [31]. Additional modules consisting of a coil immersed in an ice trap which permits condensation of the vapour formed in the microwave oven and a gas trap permitting degasification of the digested samples have been proposed [34].

7.7 SPECIATION ANALYSIS

Flow injection manifolds have been used for the discrimination between the same element in different oxidation states (e.g. Cr(III) and Cr(VI), Fe(II) and Fe(III)) or in different forms (e.g. Hg^{2+} and HgMe^+) and have been reviewed [35]. They are based on the fact that one of the forms is retained on a microcolumn whereas the other passes unretained to the detector. Injection of a suitable eluent allows the second form to be eluted out of the column and then to be carried to the detector so that the consecutive peaks are registered (Fig. 7.5(a)) [36]. In another kind of method the sample is split into two streams, one of which is subject to *on-line* reduction/oxidation. Consequently the total metal content and one form of the metal produce separate peaks (Fig. 7.5(b)) [37,38].

7.8 CALIBRATION

The standard addition manipulations and internal standardization required can be simplified significantly and completed within a shorter period of time with much less sample with an FI system [39]. A flow-injection system with a merging zones configuration and zone sampling was used for the implementation of the generalized standard additions method [40]. The use of FI techniques for calibration strategies has been reviewed [41]. Calibration in FAAS using a single standard and a gradient technique [42] and automatic sample handling and calibration methods for analysis by FAAS using discontinuous flow analysis have been discussed [43].

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Quality assurance in trace analysis

The term *quality assurance* is defined as a system of activities whose purpose is to provide, with a stated level of confidence, the assurance that the result obtained meets a defined standard of quality. The term embraces quality control (defined as the overall system of activities to control errors during the analytical procedure) and quality assessment (the mechanism to verify that the system is operating within acceptable limits). The concepts have been broadly reviewed [1–5].

Errors in trace analysis can be random which are controlled by precision (*cf.* Section 4.1) or systematic (associated with accuracy, i.e. the agreement between the true value and the obtained result). Errors can occur at all steps of the analytical procedure including sampling, sample handling prior to measurement and determination. The most common sources of error include calibration errors (wrongly prepared standards), additive interference, i.e. losses and contamination (mostly during sampling and sample handling) and spectral overlaps and multiplicative interferences (matrix suppression or enhancement). The issues of accuracy in analytical chemistry have been discussed [6,7]. The interferences occurring with different measurement techniques were discussed in Chapter 4.

8.1 STANDARD SOLUTIONS

8.1.1 Aqueous standards

Relatively concentrated stock solutions (for the sake of convenience 1 mg ml^{-1}) are prepared from the pure metals or of their simple salts. High purity metals in the form of a rod or wire are preferred as thus

problems related to uncertain stoichiometry and moisture content are eliminated. The recommended recipes for the preparation of stock solution have been summarized [8]. Prior to use stock solutions should be standardized by an absolute method, e.g. gravimetrically or coulometrically. Alternatively, stock standard solutions can be purchased from various manufacturers, also in various matrices. Stock solutions, acidified to prevent hydrolysis, may be stored for several months. Stock solutions are diluted to form working standards. Dilute standards ($<1 \mu\text{g ml}^{-1}$) should always be prepared just before use as otherwise adsorption of ions or reduced species onto the container walls is likely to occur in some cases. Special precautions and requirements, if necessary, for handling standard solutions of particular elements are discussed elsewhere in Part III. Whereas for routine work analytical grade reagents are quite sufficient, solutions with a high degree of purity, especially with respect to the analyte, are required for matrix interference studies. Unless specially prepared, commercial reagents are likely to contain many impurities at the ppm and sub-ppm level which makes them useless, for example for studies of matrix related spectral interferences. The growing popularity of simultaneous multielement techniques requires multielement standards. Their preparation requires an especially careful selection of initial reagents to avoid mixtures likely to react and cause precipitation.

8.1.2 Non-aqueous standards

When determinations are carried out in organic liquids, standards are prepared by dissolving suitable organometallic compounds in the same solvent. The solvent considerably influences atomization and thus sensitivity and analytical precision. The most suitable organic solvents for FAAS are C_6 or C_7 aliphatic esters or ketones and C_{10} alkanes. For work with plasma some aromatic compounds such as xylene are recommended.

8.2 CONTAMINATION

Contamination is defined as the addition of the analyte, in an uncontrolled way, to the sample prior to the measurement. The sources of contamination include airborne dust, water, reagents and container impurities. Contamination occurs at all steps of the analytical procedure including sampling. The blank value is a useful measure to control

contamination, however, it does not correct for sampling errors and at very low levels matching the conditions may be difficult especially with respect to airborne contamination and container impurities. A high blank primarily affects the reproducibility and the limit of detection. A prerequisite to analyze the sample should be a full knowledge of its history and the analyst is strongly recommended to assist at sampling. Contamination in trace analysis has been the subject of several reviews [8–15]. General aspects are discussed below whereas some specific issues are discussed in Parts II and III.

Airborne contamination is particularly cumbersome for elements such as Si, Al, Fe, Ca, Na, K, Mg, Ti, and also Pb, V, Zn, Ni, Cr, Cu which are common in the atmosphere, especially in densely populated areas. Additional airborne contamination due to earlier activities in the laboratory is likely to arise. The use of a clean laboratory flushed with air filtered through high efficiency particulate (HEPA) filters and accessible only through airlocks, with special dust-free protective clothing is essential for ultratrace analysis [14,16]. Vertical laminar flow clean benches are recommended in particular for the most critical work regarding contamination problems and evaporation. Activated charcoal filters are required to remove metallic gases (mercury) and metals present in the gas phase (e.g. tetraalkyllead). The purity of air is expressed by the number of particles with a diameter between 0.5 and 5 μm per cubic foot of air. Class 100 is typical (less than 100 particles) but class 10 is also used.

The analyst is an important source of contamination unless he or she wears full clean room clothing and gloves to prevent contamination from clothing, shoes, hairs and bare hands.

Water is commonly added to the sample at various stages of an analytical procedure. The water purification installations include high purity mixed bed ion exchange resins (e.g. Milli-Q systems). An alternative is water from subboiling quartz or Teflon stills.

Reagent blanks can be minimized by minimizing the amount added. High purity reagents do not always meet the required standards as the attested values are usually restricted to a few elements and sometimes are not accurate. Acids are mostly used and it is recommended that they be laboratory prepared by subboiling distillation. Infrared heating is used to avoid aerosol spraying during violent boiling [17,18].

The containers are an important contamination source because of adsorption–desorption of the material on the container surface. Polyethylene is a common material of choice but it cannot be used in contact with concentrated HNO_3 or at temperatures higher than 60°C. For

these applications PTFE can be used. Quartz is definitely the best material because of its slight tendency to adsorb and high resistance to heat but it is fairly expensive and fragile. Glass should not be used in lower trace work. Regardless of the materials used the surface needs to be preconditioned to minimize adsorption and desorption. The procedure used by NIST and adapted by many trace laboratories has been described [14,16]. Small quartz vessels are preferably cleaned by steaming the vessel with ultrapure HNO_3 or HCl in a closed circuit [19].

8.3 LOSSES

Loss of the analyte may occur at all steps of the analytical procedure leading to negative errors unless corrected for. Several categories of losses can be distinguished. As in many cases losses are difficult to control and random precautions may need to be taken to avoid them.

Adsorption losses occur as a result of the reaction of the analyte with the wall of the sampling or storage container or the reaction vessel in a random way. Preconditioning of the container as described above minimizes the adsorption losses. The adsorption can be further reduced by using round bottom vessels (lower surface area) and larger sample amounts. At high decomposition temperatures, elements in the sample can be irreversibly bound to the vessel surface. Adsorption losses are particularly acute for sparingly soluble products present in the sample or formed during the chemical treatment, e.g. oxides, phosphates, silicates.

Spray losses usually occur when gas is evolved during dissolution as a result of either a chemical reaction or too violent boiling. A small part of a hot solution is carried away as spray. Spray losses occur randomly and should be minimized by using infrared heating and mild reaction conditions.

Volatilization losses are the most common especially for decomposition in open vessels and concern volatile chlorides of, for example Hg(II) , Sb(III) and As(III) . In addition Cr(III) can be lost from HClO_4 at temperatures above 150°C through formation of chromyl chloride. When metals are dissolved in non-oxidized acids, some elements such as As, Sb and S may escape as hydrides. Losses caused by volatilization are fairly irreproducible and should be avoided by using closed systems for decomposition.

Process losses result from non-quantitative extraction, preconcentration or sorption yield and are fairly reproducible, thus allowing correc-

tion, e.g. by standard addition (*cf.* Section 5.2). Both random and systematic losses can be corrected for by isotope dilution analysis (*cf.* Chapter 5.2) provided that the enriched spike is added at a sufficiently early stage of the procedure and is well equilibrated.

8.4 ACCURACY VERIFICATION

Recovery studies are based on adding a small quantity of pure analyte (the spike) to a sample in which the concentration of the analyte has already been determined or is known to be zero and determining the spike after it has passed through all the analytical procedure. Synthetic samples, formulated from known quantities of constituents in such a way as to match as closely as possible the real samples, can also be used to determine the percentage yield of the analyte. Very efficient is the use of radioactive tracers. Recovery studies are a convenient way to localize losses but must not be regarded as a definitive proof of accuracy as it is very common that the analyte species actually present in the sample will behave in a totally different way from the spiked form.

Definitive analytical methods. In an absolute sense the true value can be defined only as being that value directly traceable to the base system of measurement units or their derivatives. More generally, ISO defines traceability as the property or result of a measurement whereby it can be related to appropriate standards, through an unbroken chain of comparisons [20]. The absolute methods include gravimetry and coulometry. In trace analysis isotope dilution MS (*cf.* Section 5.4) is the most common definitive method.

Interlaboratory comparisons (round-robin exercises) are a valuable supplement to internal quality control and are essential for the method of development and certification of certified reference materials (CRMs) (for particular materials and elements see elsewhere in Parts II and III, respectively).

Certified reference materials are reference materials in which one or more element concentrations are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body [21]. Many materials for specific materials are listed in Part II. More detailed information can be obtained from institutions such as the National Institute of Standards and Technology (NIST, USA), formerly NBS, National Research Council of Canada (NRCC), National Institute for Environmental Studies

(NIES, Japan), International Atomic Energy Agency (IAEA, Austria) and Bureau Communautaire de Référence (BCR, EU). Criteria for developing reference materials, methods of certification, contents of certificates and their use have been extensively discussed [21–25]. An international database of CRMs has been assembled [26]. An extensive compilation of NBS CRMs has been published [27]. Recent BCR projects have been discussed [28]. Quality control in speciation investigations has been discussed [29].

The only rational basis for using an RM is to monitor a measurement system that is in a state of statistical control. The major use and indeed the original driving force behind CRM development is the quality assurance of measurement processes. CRMs are often used in the development and calibration of reference methods and ensuring their accuracy. Secondary in-laboratory reference materials can be produced to be used on a routine basis.

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Environmental and geological materials

9.1 AIR

Analysis of air is essential for industrial hygiene, environmental quality and global change studies [1–4]. At the workplace elevated concentrations of metals may occur as a result of abrasive blasting, cleaning of metals and painting. Exposure limit standards exist for most elements, especially As, Sb, Be, Ag, Sn and their compounds. Airborne emissions from industrial processes, power and incineration plants, combustion and all types of mobile sources affect the environment and are subject to continuous monitoring in industrial and urban areas. Emissions from natural sources (biogenic, marine or volcanic) also contribute to the atmospheric levels of metals and metalloids.

From the analytical point of view air is operationally divided into a gaseous phase (passing through a 0.45 μm filter) and a particulate phase (retained on the filter). The latter usually includes aerosols but in extremely polluted areas dust and fly ash (*cf.* Section 9.4) can constitute a dominant fraction. The gaseous phase contains metallic compounds with high vapour pressure (e.g. Hg), covalent compounds (e.g. AsH_3 or SbH_3) and organometallic species, either fully covalent (e.g. Et_4Pb) or ionic (MeHg^+ , trialkyllead). Analysis for particular gaseous species is discussed in relevant chapters in Part III. Multielement methods are usually applied to particulate matter which may contain a large number of elements of widely different concentrations and variable amounts of organic material and silicate-based dust. The principal problems include representative sampling and control of the blanks (especially when dissolution of the filter is necessary). Analysis of air has been reviewed extensively with emphasis on the particulate fraction [5–10]. Physical and chemical characterization of individual particles has been discussed [11].

9.1.1 Sampling and sample handling

Sampling

Ambient aerosols are characterized by particle size range, from 0.45 μm (filter cut-off) to more than 10 μm , and chemical composition. The aerosols are usually collected by filtration, impaction, or electrostatic precipitation. Samplers have been designed to separate inhalable or respirable ($<2.5 \mu\text{m}$), coarse inhalable (2.5–10 μm) and non-inhalable particles ($>10 \mu\text{m}$). If the total ambient concentration of the elements is of concern, the airborne particles are generally collected by filtration [12,13] of a known volume of air pulled for a preset time. Choice of filters is critical with respect to particle size, collection efficiency and likely contamination [8]. Glass fibre filters have high efficiencies but are heavily contaminated and have too high a background for NAA. The best choices for high volume sampling are cellulose or quartz membrane filters owing to their purity, low pressure drop, low cost and ease of handling. Particle size differentiation is possible using sequential filtration or size-selective inlets for the classical high volume samplers so that an upper cut-off is established [14]. More detailed information on particle size distribution can be obtained with inertial cascade impactors [15–18] of which many types are commercially available. Long sampling periods are often required for membrane filters to obtain measurable amounts of analytes so that the methods are retrospective and not exclude the possibility of an ingestion of a short, accidental exposure. Collection of aerosol on a graphite rod or tube by inertial impaction or electrostatic precipitation was proposed to enable near-real-time determination of metals in aerosols [19–22]. Personal samplers used for monitoring dusts and aerosols in work places have been discussed [23–26]. The most common sampler consists of a two- or three-piece filter cassette containing a 0.8- μm pore size mixed cellulose ester membrane filter supported by a cellulose backup pad. The cassette is placed within the breathing zone of a worker while air is pulled by means of a personal pump.

Digestion of filters

In many methods the filter with the collected particulate material is digested or leached. Various decomposition and leaching procedures involving the use of HNO_3 [18], or acid mixtures such as, *aqua regia* [27–29] or $\text{HNO}_3\text{--HClO}_4$ [28] have been proposed. To ensure the decomposition of the aerosol aluminosilicate matrix (that might otherwise

trap, for example Al, Fe and Ti) an HF treatment has to be included [27–29]. The presence of HF hampers the determination of Mg [28] and attacks quartz carriers for TXRF [17]. For some easily soluble elements (e.g. Pb, Cd) extraction with dilute acid may be sufficient. Volatile elements require a reflux [29]. Microwave digestion is recommended to speed up the dissolution and to improve the yield [29]. Pressure bomb digestion alleviates contamination problems [30]. Some procedures involve fusion of the filter with alkalis or Na_2CO_3 followed by dissolution in acid which is not applicable for Cu, Pb, Cd and Zn because of volatilization losses and generally results in high salt content and blanks [31]. Different methods for filter dissolution have been compared [28,31].

Separation and preconcentration

The removal of the silicate matrix is essential to increase the stability of the sample solution and to avoid the precipitation of silicate. Loss of certain elements (Si, B, As, Be, Sb) as volatile fluorides is a well known limitation when HF is used for the sample digestion (*cf.* Section 3.1). Boric acid can be used to complex fluoride remaining after digestion with HF [32].

9.1.2 Analysis

The most popular is multielement simultaneous analysis of the filter without digestion, by XRF [33] or INAA [12,34–38]. As no chemical step is involved a detailed discussion is beyond the scope of this book. The increasing popularity of TXRF is worth emphasizing [16–18]. Instrumental NAA is especially well suited for atmospheric aerosols collected on a clean organic filter which support does not produce significant γ -activities. The most abundant aerosol matrix elements (Si, Al, Fe, Ca, Mg and Cl) are not readily activated either. The high Na content of marine aerosols can give rise to a troublesome ^{24}Na ($t_{1/2} = 24$ h) activity whereas ^{82}Br ($t_{1/2} = 36$ h) may interfere in urban aerosols.

Filters can be directly introduced into a plasma or a GF atomizer but elevated background problems, calibration difficulties, microweighing errors and sample representativity are hampering factors for reliable results to be obtained [39,40]. Once destroyed, the filter collected material can be analyzed by virtually any spectrometric technique; ICP AES [41–43] and ICP MS [30] are favoured. Where high sensitivity is essential and the number of elements to be determined is not very large, GF

AAS is recommended. It is usually applied for heavy metals (Pb, Cu, Cd, Tl) or hydride forming elements (Sb, As). In combination with a single-stage impactor the ng/m^3 levels can be determined in a direct and nearly-real-time manner [19,44,45]. The graphite furnace can also serve as an impactor surface itself for air particulate offering a significant intrinsic preconcentration factor [46]. Different atomic spectroscopic techniques have been discussed with special emphasis on AAS [47–49]. Analytical methods (involving a chemical handling step) applied to the analysis of the air particulate fraction are summarized in Table 9.1.

9.2 WATER

Water is analyzed for the purpose of biogeochemical studies and natural resource monitoring for anthropogenic pollution [56]. Water samples are divided in several classes which differ in terms of trace metals, salt and suspended particulate content. *Fresh waters* which include continental river, estuarine and lake waters are analyzed for pollution by heavy metals in order to assess the self-purification power and the net pollutants discharge into the sea. Fresh waters are rich in particulate matter, Mg and Ca (hardness) and contain moderate concentrations of trace ions complexed by humic substances which vary with depth, salinity and the proximity to discharge points. Possible species present in fresh water have been summarized [57]. *Seawater* is essentially a fairly concentrated salt solution with Na^+ , Mg^{2+} , Ca^{2+} and K^+ as predominating cations and chloride and sulphate as major anions [58]. The concentrations of carbonate and bromide are distinctly smaller but large enough to influence the speciation of elements. The average pH is *ca* 8 and may vary with depth, temperature and location. Suspended particulate matter and marine organisms are naturally present. *Mineral and hydrothermal waters* are associated with various types of rocks and a whole range of leached elements (e.g. Li, B, Ga, Ge, Rb, Cs, W) the concentration pattern of which can be used for the source fingerprinting and prospecting studies. *Atmospheric precipitation* (rain, snow, sleet) is a primary mechanism by which most metals are removed from the atmosphere onto the ocean and land. The need for analysis is driven by pollution concerns and interest in global elemental biogeochemical cycles. Heavy, alkali and alkaline earth metals and some anions (NO_3^- , SO_4^{2-}) are usually determined. The samples are slightly

TABLE 9.1

Multielement trace analysis of air particulate fraction

Sampling technique	Digestion	Elements determined	Detection	Ref.
Impaction	HNO ₃ (bomb)	As, Cd, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Pb, Sb, Se, Ti, V, Zn, Zr	TXRF	18
Impaction	HNO ₃ -HCl-HF	Al, Cd, Cu, Fe, Mn, Na, Zn	FAAS, GF AAS	50
Impaction, membrane filter	HNO ₃ or cool plasma dry ashing	Ba, Ca, Cr, K, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Pb, Ti, V	TXRF	17
Glass fibre filter	HNO ₃ , HClO ₄ -HF	Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Zn	ICP AES	42
Glass fibre filter	HF	Cr, Mn, Pb	ETV ICP AES	51
Quartz filter	HNO ₃ -H ₂ SO ₄ -HF (slurry)	Sb, Ni, V	GF AAS	39
Quartz filter	fumed off with HF, HNO ₃ -HF (bomb)	As, Sb, Se, Tl	GF AAS	32
Quartz filter	HF, HNO ₃ -HClO ₄ (bomb)	Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Sr, V, Zn	ICP AES	41
Cellulose acetate filter	slurry in 1% HNO ₃	Cd, Cu, Ni, V	GF AAS	40
Cellulose acetate filter	slurry in 1% HNO ₃	Fe, Mn, Pb	FAAS	40
Nitrocellulose filter	fusion with Na ₂ CO ₃ -H ₃ BO ₃	Al, Ba, Ca, Cr, Fe, Mn, Mg, Si, Ti	FAAS	52
Nitrocellulose filter	HF-HNO ₃ -HCl	Cd, Co, Cu, K, Li, Na, Ni, Pb, V, Zn	FAAS	52
Polycarbonate membrane filter	HNO ₃ -H ₂ O ₂ (bomb)	As, Cd, Co, Cu, Fe, Mn, Ni, Pb	GF AAS	53
Membrane filter	H ₂ SO ₄ -HNO ₃	Cr, Cu, Ni	ICP AES	43
Membrane filter	HF-HClO ₄ -HNO ₃	Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sb, Sr, Ti, V, Zn	ICP AES, GF AAS	54
Teflon membrane filter	HNO ₃ -HF-H ₂ O ₂ , microwave assisted	As, Cd, Mn, Ni, Se, V	GF AAS	55
Teflon membrane filter	HNO ₃ -HF-H ₂ O ₂ , microwave assisted	Al, Ca, Cu, Fe, K, Mg, Na, Pb, Si, Zn	FI AAS	55

acidic, poor in salts and particulate matter and show variable concentrations of most components in space and time. *Tap* (drinking) water is subject to precise norms determining the allowed contents of trace elements [59]. It is free of particulate matter and contains antibacterial preservatives (chlorine). Because of the need for accuracy the analysis should ideally be carried at a level 10 times higher than the actual detection limit. *Wastewaters* include industrial discharges and municipal sewage and effluents. The composition is dependent on the plant. The toxic metal levels are normally significantly higher than in natural water. *Brines* are waters with extremely high (above 10%) salt (NaCl, KCl) content. They can be natural (Dead Sea) or industrial (desalination plants). *Interstitial waters* which play an important role in the transport of trace elements from the sediment–soil to the over- or underlying water and conversely are usually isolated by centrifugation in the presence of a displacing agent (inert, dense water-immiscible fluorocarbon solvent). In some pore water samples rich in Ca and Mg, precipitation of carbonate minerals may occur during centrifugation and filtration owing to degassing of dissolved CO₂ and the accompanying pH increase which seriously affects trace element speciation [60].

9.2.1 Sampling and storage

Sampling has been discussed in detail for natural waters [61,62] and seawater [63]. It must be considered in terms of avoiding contamination and sampling strategy (representativeness) [64,65]. Polyethylene or polycarbonate bottles are recommended for all metals other than Hg for which the requirements are discussed in Chapter 36. Cleaning protocols are extensively described elsewhere (*cf.* Section 8.2) and may be more or less diligent depending on the concentrations and elements determined.

Sample collection

Surface waters should be collected by means of a sample bottle at the end of a telescopic bar container, from a rubber boat rowed upstream to avoid contamination from the boat itself. For surface water sampling, immersion of a polyethylene sampling bottle to well below the surface to avoid any surface boundary layer at which trace metals accumulate is generally adequate [66]. Conventional sampling of deep waters by clamping samplers to a hydroline is not appropriate for trace metal analysis because of the severe contamination hazard which can only

be avoided by using a plastic coated hydrowire and a number of special precautions [67]. Pumping systems offer a valuable alternative for shallow waters (<100 m), although the higher surface-to-volume ratio may enhance the possibility of contamination. For the collection of discharge waters flowing in pipes or channels, it is important to establish experimentally the homogeneity of the trace element distribution; sampling from the edges, surfaces, or bottom of discharge channels should be avoided. For the collection of tap water the first water running from the tap must be avoided because there will be a high accumulation of trace metals stemming from the pipes, soldering and welds. Automatic samplers can be connected via a bypass to the water mains. Rain and snow are collected with an automated sampler which restricts sampling to precipitation periods, thus eliminating interference from dry deposition. A suitable sensor opens or closes the cover depending on the humidity [67a].

Filtration

Filtration or centrifugation is required for a differentiation between the total element (including particulate-bound fraction) and the dissolved element contents. It is also used as a routine measure prior to sample storage. In unfiltered samples high bacterial concentrations associated with sedimentary material will lead during prolonged storage to depletion of soluble metal species and changes in the CO₂ concentration (and thus the pH), and consequently may result in precipitation, changes in the degree of complexation and the distribution of chemical forms of elements in solution. Immediate field filtration is recommended but is contamination prone. A 0.45 µm membrane filter is assumed to separate any insoluble material. Polycarbonate or cellulose filters are preferred to glass filters owing to low affinity to heavy metals and easier cleaning. Centrifugation can be a useful alternative for difficult-to-filter samples.

Storage

The sample should be stored chilled (not frozen) to about 4°C to retard bacterial growth. For the same purpose, preservative reagents may be added. It is recommended that the sample be acidified as soon as possible after collection to prevent losses of metals from dilute aqueous solutions. Samples of unknown origin should be treated with caution for the possibility of liberating highly toxic H₂S or HCN. The choice of storage container is determined by both its adsorptive proper-

ties and the presence of surface impurities (*cf.* Section 8.2). Soda glass containers which can act as weak ion exchangers should be avoided. Both polymers and glass may contain heavy metal impurities capable of contaminating the sample. Special care for Hg, As, Se, Ag and organometals is discussed in Part III.

9.2.2 Preconcentration

Any separation/preconcentration step makes the analytical procedure longer, prone to contamination and losses because of unknown speciation and should not be used in routine analysis at higher than $50 \mu\text{g l}^{-1}$ levels albeit that a plethora of relevant methods have been published. If elements are likely to occur as complexes the sample should be digested prior to preconcentration owing to the uncertainty of speciation.

Evaporation

Evaporation is the simplest preconcentration method but it is prone to spray losses unless infrared surface heating or rotary evaporation is employed. Alternatively, freeze drying can be used [68–70]. Matrix salts are co-preconcentrated leading to salt rich solutions. The dry residue from fresh water consists generally of carbonates, sulphates, nitrates and chlorides. Chlorides and nitrates are hygroscopic and impossible to manipulate in practice. A phosphate medium is more suitable; H_3PO_4 or KH_2PO_4 is added to the water to be analyzed prior to lyophilization [70]. Adsorbed material, especially iron, is often difficult to desorb even after prolonged heating with acids. The usual preconcentration factors are 5–10. In ultratrace analysis the process must be carried out in a clean bench [71]. Evaporation is commonly used prior to TXRF or NAA analysis.

Solvent extraction

Solvent extraction offers a preconcentration factor of 10–20 on a routine basis which can amount up to 250 in some cases. Group extraction (Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn and some others) with dithiocarbamates (APDC, DDTC) into various organic solvents is the most widely used. The main matrix elements: Ca, Mg, Na and K are not extracted. APDC is more suitable than DDTC especially at low pH values. A mixture of both makes the pH range for quantitative extrac-

tion broader [72,73]. Other dithiocarbamates [74–75], have been proposed, usually in mixture with APDC. Back extraction into diluted HNO_3 or (faster) with Hg(II) solution is applied to avoid volatilization losses during drying and ashing steps in GF AAS or plasma disturbance [72,73,76]. Alternatively, extracts can be evaporated to dryness, the residue being mineralized with HNO_3 and redissolved [77,78]. Extraction suffers from a fairly poor preconcentration coefficient, variable blanks, and poor perspectives for automation but it can be applied to unfiltered samples. Extraction is excellent for use with spectrophotometry or flame AAS.

Ion exchange

Chelating resins are preferred to simple ion exchangers because of high selectivity for transition metals *vs* alkali and alkaline earth cations and multielement capability under the same conditions. Large concentration factors can be obtained but high and variable blanks (especially for Zn and Fe) are common. The most widely used resins are Chelex-100 and those containing the hydroxyquinoline group. Sorption of trace elements on Chelex-100 has been studied exhaustively [79]. The sorbent is very efficient in the batch mode (0.4 g of resin is sufficient for 1 l of sample) whereas in column mode low flow rates ($1\text{--}2\text{ ml min}^{-1}$) and low enrichment factors (<20) are a drawback [79–80]. Chelex-100 fails for solutions rich in Fe, Ca and Mg (e.g. seawater) which elements compete for adsorption sites with trace analytes. For the removal Ca and Mg careful washing procedures (e.g. with ammonium acetate) are required [79,80]. Efficiency is also reduced for aged acidified samples [81] and some waters with complex speciation of heavy metals [82]. The optimal pH for column operation should be 6–7 and is strongly affected by the salt matrix [82]. 8-Hydroxyquinoline immobilized on silica shows an advantage over Chelex-100 in *on-line* systems in terms of resistance to swelling with changes in solvent composition [83]. 20–50-fold preconcentration factors at pH 7–8 are routine [83–85] but factors up to 500 can be achieved [86].

Sorption

Sorption of various analyte complexes, usually oxinate or dithiocarbamate on C_{18} -bonded silica gel with subsequent elution with methanol is becoming popular. Enrichment factors of 50–100 can be obtained and the column may be reused repeatedly in a FI system [87,88]. Alternatively, other complexing agents, e.g. dibenzyl–DTC complexes [68,89],

bis(2-hydroxyethyl)-DTC [90,91], APDC [92] on Chromosorb [68–89] and Amberlite XAD-4 [90–93] have been used. Sorption of several non-complexed metal cations on Amberlite XAD-7 followed by elution with 1% HNO_3 has been reported [94]. Other sorbents used have included lipophilic cyclic tetramines impregnated on XAD-7 or XAD-4 [95], Cellulose–Hyphan [96] and many others, usually of transient importance. Integrated *in situ* sampling–preconcentration units where water is drawn at a constant rate through a sorbent column for a fixed time interval are becoming popular [97].

Precipitation

Most elements except alkali and alkaline earth metals are precipitated from acid and slightly alkaline media in the presence of a suitable carrier and/or a complexing reagent (*cf.* Section 3.2.1). Acids and ammonia are used for pH adjustment since they are easily purifiable. Hydrated Fe(III) oxide is very popular (Fe(III) is usually naturally abundant in the sample) but suffers from problems during filtration. Gallium causes very few spectral interferences and is available in high purity but cannot be applied to fresh waters because $\text{Ga}(\text{OH})_3$ does not precipitate (pH 9) in the absence of Mg [98,99]. Coprecipitation with Zr at pH 4 gives a good quality of precipitates for filtration but it was limited by spectral interferences in ICP AES and the refractory character of Zr in AAS [100]. Magnesium present in seawater and brines is a good carrier in the pH region between 8 and 9 for several metal cations and also B and Si. Reductive precipitation is used for several metals (Au, Cd, Co, Cr, Hg, Ni, Pb, Pt, Sb, Sn, Tl, V and Zn) in the presence of iron and/or palladium as carrier(s). The precipitate is filtered off and redissolved in a mixture of HNO_3 and HCl. Some elements (As, Pb, Sb, Se and Sn) may be lost from solution as volatile hydrides. Palladium is used as a carrier since it is easily precipitated in the elemental form, it is seldom an analyte of concern in water analysis and it is a convenient matrix modifier in the GF AAS determination of As, Bi, Se, Sb, Sn and Te [101]. The presence of iron results in granular precipitates that are easy to handle and filter [102] and improves recoveries for As and Sb [101]. Organic precipitating agents, e.g. 8-hydroxyquinoline in the pH range 7–8.5 [103], APDC (2% HClO_4) [104,105] and dimethylglyoxime-PAN [106] are recommended as the precipitate does not introduce its matrix. The precipitate can be analyzed directly; the elimination of the need for redissolution increases the preconcentration factor.

9.2.3 Determination techniques

Analytical techniques for water analysis have been discussed [107–110]. The most versatile is ICP MS of which wide implementation is hampered by high investment and running costs. For alkali and alkaline earth metals and some heavy metals (Cd, Co, Cu) the position of AAS and ICP AES is very strong. When preconcentration step is allowed, TXRF becomes successful. The performances of ICP MS, ICP AES, ICP AFS and FAAS for the multielement analysis of natural waters has been compared [111]. Systematic separation and determination of some nuclides (Rb, Au, Sc, Y, Tb, Tm, Lu, Hf, Nb, Ta, Co, Ni, U, Pu, Am, Cm) in fallout samples has been discussed [112]. Analytical procedures for the analysis of waters are summarized in Table 9.2.

TABLE 9.2

Multielement trace analysis of water after preconcentration

Water	Preconcentration	Elements determined	Detection	Ref.
Drinking (0.1 l)	sorption on Chelex-100; elution with HNO_3	Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Mg, Mn, Ni, V, Zn	ICP AES	96
Drinking (0.35 l)	extrn. with PMDTC (MIBK)	Cr, Fe, Mn, Ni	FAAS	75
Drinking (2 l)	sorption of oxinate complexes on poly(chloro- trifluoroethylene)resin	Cu, Fe, Mn, Ni, Zn	FAAS	113
Drinking (5 ml)	sorption of oxinate complexes on C_{18}	Ag, Al, Cd, Cr, Fe, Mn, Ni, Pb	FAAS	114
Drinking, sea (0.5–1 l)	copptn. with TAN, APDC and ammonium N-nitroso- phenyl-hydroxylamine	Cd, Co, Cu, Hg, Mn, Th, U, V, Zn	INAA	115
Drinking, fresh, sea (0.15 l)	copptn. with APDC	Cd, Co, Cu, Mo, Ni, Pb	ICP AES	116
Drinking, fresh, sea (0.15 l)	copptn. with APDC; dissoln. in HNO_3	Cd, Co, Cu, Pb, Mo, Ni	ICP AES	104

continued

TABLE 9.2 (continuation)

Water	Preconcentration	Elements determined	Detection	Ref.
Drinking, fresh, sea (0.5 l)	extrn. with DDTC (CCl ₄)	Cd, Co, Cu, Fe(III), Ni, Pb	GF AAS	77
Fresh (2 l)	sorption of APDC complexes on Amberlite XAD-4, elution with acetone	Cd, Co, Cu, Fe, Mn, Ni, Pb	FAAS	92
Fresh (0.75 l)	sorption on Chelex-100; elution with HNO ₃	Cd, Cu, Pb, Zn	ICP AES	117
Fresh (0.01–0.08 l)	sorption on a chelated ion-exchanger column of SO ₃ –oxine CM–cellulose	Cd, Co, Cu, Mn, Ni, Pb	FIA ID ICP MS	118
Fresh (0.3 l)	sorption on silica-immobilized 8-hydroxyquinoline, elution with HCl–HNO ₃	Cd, Co, Ni, Pb	ICP MS	71
Fresh (0.01 l)	sorption on silica-immobilized 8-hydroxyquinoline, elution with HCl–HNO ₃	Cd, Mn, Mo, U	ID ICP MS	83
Fresh (1 l)	sorption on functionalized polystyrene resin, elution with HCl	Cu, Fe, Mn, Pb, Zn	GF AAS	119
Fresh (2.5 l)	extrn. with APDC/DBADBDC (2-ethylhexyl acetate)	As, Cd, Co, Cr(III,VI), Cu, Fe(II,III), Mn, Mo, Ni, Pb, Se, Sn, Pb, V, Zn	ICP AES	74
Fresh (0.1 l)	sorption on Chelex-100, C18, Fractogel DEAE	Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn	ICP MS	120
Fresh (0.25 l)	copptn. as piperazino-1,4-bis(dithiocarbamate)s	Co, Cu, Fe, Ni, Zn	ED XRF	121
Fresh (0.25–1 l)	copptn. with Cd/APDC	As, Cu, Fe, Ni, Se, Pb	XRF	105
Fresh (0.2–0.5 l)	copptn. with Bi, Pb-APDC	Cd, Co, Mo, Se, Ti, V	INAA	122
Fresh (0.4 l)	copptn. with oxine	Cd, Pb, Zn	GF AAS	123

Water	Preconcentration	Elements determined	Detection	Ref.
Fresh, CRM (0.075 l)	sorption as butane-2,,3-dione bis(N-pyridinoacetyl hydrazone) complex on Amberlite XAD-4, elution with HNO ₃	Cd, Co, Cu, Ni, Pb	ICP MS	124
Fresh, sea, CRMs (0.025 l)	sorption on a iminodiacetate resin	Co, Cu, Mn, Pb, Zn	FI ICP MS	125
Fresh, sea (0.03 l)	sorption on XAD-4 resin as HEDC* complexes	Cd, Cu, Ni, Zn	GF AAS	91
Fresh, sea	sorption on an iminodiacetate resin, cation exchange	Cd, Cu, Fe, Mn, Zn	VIS	126
Fresh, sea (0.01–0.35 l)	copptn. as PAN complex with Ni dimethylglyoximate	Cd, Co, Cu, Fe, Mn, Pb, Zn	GF AAS	106
Fresh, sea (0.1 l)	extrn. with Kelex 100 (toluene)	Cd, Cu, Mn, Ni, Pb	GF AAS	76
Sea (up to 0.12 l)	sorption of oxine complexes on Amberlite XAD-2, elution with 2 M HNO ₃	Cd, Cu, Fe, Mn, Ni, Zn	ICP AES	93
Sea (0.05 l)	sorption of bis(carboxymethyl)-dithiocarbamate complexes	Bi, Co, Cr, Cu, Hg, Mo, Ni, Pt, V	ICP MS	127
Sea (0.2 l)	sorption of DBDC complexes, elution with CHCl ₃ –MeOH	Cu, Fe, Kg, Mn, Mo, Ni, Pb, U, V, Zn	TXRF	89
Sea (0.5–1 l)	sorption on Chelex-100, elution with 2.5 M HNO ₃	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	GF AAS ICP AES	80,81 128
Sea (0.2 l)	sorption on Amberlite XAD-7, elution with HNO ₃	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	GF AAS	94
Sea (1 l)	sorption on cellulose–Zn(OH) ₂	Cd, Cr, Cu, Fe, Hg, La, Ni, Pb, Sn, V	ICP AES	129

continued

TABLE 9.2 (continuation)

Water	Preconcentration	Elements determined	Detection	Ref.
Sea (0.1 l)	sorption on silica-immobilized 8-quinolinol; elution with HCl-HNO ₃	Cd, Cu, Ni	ICP AES	130
Sea (0.5 l)	sorption on silica-immobilized 8-quinolinol; elution with HCl-HNO ₃	Cd, Co, Cu, Mn, Ni, Pb, Zn	ICP MS	86
Sea (2 l)	sorption on silica-immobilized 8-quinolinol; elution with HCl-HNO ₃	Cd, Cu, Mo, Ni, Pb, U, Zn	ID ICP MS	84
Sea (0.8–5 ml)	sorption on silica-immobilized 8-quinolinol; elution with HCl-HNO ₃	Cd, Cu, Fe, Mn, Ni, Pb, Zn	FI GF AAS	131
Sea (0.5 l)	sorption on 7-dodecenyl-8-quinolinol loaded resin	Cd, Cu, Fe, Mn, Ni, Pb	GF AAS	132
Sea (2 l)	sorption on Chelex-100, elution with HNO ₃	Cd, Cu, Pb	GF AAs	72
CRM sea (0.01 l)	sorption on a chelating ion exchanger	Cu, In, Mo, Ni, U, Zn	ICP MS	133
Sea CRM	sorption on a chelating ion exchanger, elution with 2 M HNO ₃	Cd, Cu, Mn, Ni, Pb, Zn	GF AAS	134
Sea (0.1–0.5 l)	copptn. with 8-hydroxyquinoline	Cd, Cu, Mn, Pb, Zn	GF AAS	103
Sea (0.9 l)	copptn. with NaBH ₄ , dissolution in HCl-HNO ₃	As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se(IV), Zn	GF AAS	101
Sea (1 l)	copptn. with Zr(OH) ₄ , dissolution in HCl	Al, Cr, Cu, Fe, La, Mn, Pb, Sb, Ti, Y, Zn	ICP AES	100
Sea, hydrothermal (10 ml)	copptn. with Ga(OH) ₃ , dissolution in HNO ₃	Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Ti, Y, Zn	ICP AES	99
Sea (1.25 ml)	extrn. with APDC (1,1,1-trichloroethane)	Cd, Cu, Pb, Ni	GF AAS	135

Water	Preconcentration	Elements determined	Detection	Ref.
Sea (0.25–0.3 L)	extrn. with APDC/DDTC (CHCl ₃); back-extrn. (HNO ₃)	Cd, Cu, Pb	GF AAS	72
Sea	extrn. with DDTC-APDC (CHCl ₃); back-extrn. with Pd(II) in HNO ₃	Bi, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Zn	ICP AES	73
Sea (0.5 l)	extrn. with dithizone, mineralization of the extract with HClO ₄	Ag, Cd, Cu, Ni, Pb, Zn	ID ICP MS	136
Saline irrigation drainage (100 ml)	extrn. with APDC (CHCl ₃), evapn., dissoln. in HNO ₃	22 elements	ICP AES	78
Geothermal (up to 1 l)	copptn. with Al(OH) ₃	La, Ce, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu	INAA	137
Reactor coolant (1 l)	cation exchange	Fe, Mn, Ni, Co	ICP MS	138
Rain (20 ml)	sorption of DBDC complexes, elution with CHCl ₃ –MeOH	Cd, Cu, Fe, Mn, Mo, Ni, Pb, Se, V, Zn	TXRF	68
Rain	sorption on 8-quinolinol loaded XAD-2 resin	Cd, Co, Cu, Hg, V, Zn	INAA	139
Rain (n.g)	copptn. with Co-APDC	Cd, Cu, Fe, Ni, Pb, Zn	FI ICP AES	140
Water (100 l)	sorption on a chelating ethylcellulose	Cd, Co, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn	FI ICP AES	141
Water (2.5–25 ml)	sorption of complexes with 8-hydroxy-7-iodoquinoline-5-sulphonic acid on an anion exchanger	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	ICP AES	142
Water	copptn. with Bi ₂ S ₃	As, Mo, Sb, Se	RNAA	143

*Bis(2-hydroxyethyl)dithiocarbamate.

copptn. = coprecipitation; dissoln. = dissolution; extrn. = extraction; evapn. = evaporation.

Flame AAS is fairly versatile albeit its direct application to some elements (e.g. Al) in less polluted waters is problematic. Aluminium, silicate and phosphate interfere in an air-C₂H₂ flame by formation of involatile compounds. An N₂O-C₂H₂ flame or La addition should be used. Matrix matching is required for high salt matrices either naturally present or resulting from evaporative preconcentration. The photodissociation continuum of NaCl (especially in highly mineralized water and seawater) increases the background absorption which must be corrected at wavelengths below 360 nm. The addition of a Cs salt as the ionization buffer is required to prevent interferences for most transition metals. Flame AAS is recommended for use with the MIBK extraction step which improves the nebulization efficiency.

Electrothermal AAS offers a better sensitivity than FAAS and can be used for less polluted (treated) and surface waters. An HNO₃ matrix (0.5–1% v/v) is usually preferred. Calcium and Mg suppress the atomization of many elements whereas NaCl, sulphates and carbonates can be responsible for large non-specific absorptions. Both Zeeman and D₂ background correction systems were found to be suitable for the analysis of low ionic strength waters [144,145] but the Zeeman correction is required for seawater. Analytical procedures usually try to eliminate NaCl (at least partly) during the charring step by a slow volatilization at 950°C which works for most moderately volatile and involatile elements. For low boiling elements (Cd, Pb, Zn) the addition of matrix modifiers (NH₄H₂PO₄ or (NH₄)₂HPO₄) which, on the one hand, promote formation of NH₄Cl (which sublimates at 335°C) and on the other hand form thermostable pyrophosphates with the analytes is required. The STPF concept (*cf.* Section 4.4.3) eliminates interferences in the analysis of chloride-carbonate waters, but waters with high content of sodium and magnesium sulphates need to be diluted and even then interference remains [146]. Ascorbic acid was added to reduce matrix effects in GF AAS determination of Pb, Mn, Mo and V in seawater [147]. With the use of Pd-Mg nitrate modifier for Z GF AAS the determination of As, Cu, Mn, Pb, Sb, and Se in water is possible using the same furnace programme without any degradation in sensitivity compared with conditions optimized for each individual element [148]. Direct GF AAS for seawater analysis has been extensively discussed [149]. The applications of AAS for natural and waste waters have been reviewed [150–152]. The effect of various operational modes (direct calibration *vs* standard additions, single *vs* double injections, peak height *vs* peak area quantification) on the precision and bias of environmental trace

element analysis has been studied [153]. *In situ* preconcentration of trace metals in high purity water by multiple injection has been reported [154].

Inductively coupled plasma AES offers detection limits sufficient for the direct analysis for many elements at regulatory criteria levels set for drinking, environmental and industrial waters [155–157]. Typical problems include insufficient detection limits for less polluted, e.g. seawater samples, matrix suppression and nebulizer or torch blockage for seawater and brines, and spectral interferences. The excellent detection limits for the alkaline earth metals (Ca, Ba, Sr, Mg) make them easy to determine directly. In the case of hard waters, the presence of elements such as Al, Ca, Fe, K, Mg, Mn, Na and Si at relatively high concentrations causes “stray radiation” and/or overlap interferences. Babington or bellmouth [158] concentric nebulizers are essential for high particulate or high salt solutions. Various separation–preconcentration approaches were attempted (*cf.* Table 9.2). After extraction it is necessary to evaporate the organic solvent as this may extinguish the plasma and dissolve the residue in HNO_3 . Direct introduction of organic solvents into the plasma has been discussed [74]. Electrothermal vaporization ICP AES can be used for microinjections of polluted waters or sample loaded sorbent [159]. The bulk of the matrix is separated from the analytes by submitting the furnace to a suitable temperature regime [159]. Calibration with aqueous standards is sufficient for natural soft waters. A standard addition and/or use of internal standard is recommended for the analysis of concentrated saline solutions (e.g. brines) to correct for the differences in densities.

The high sensitivity and multielement capability make ICP MS suitable not only for the analysis of filtered natural waters and precipitation [160–163] but also for that of thermal waters [164]. For the analysis of seawater and brines, separation procedures (usually ion exchange or sorption (*cf.* Table 9.2)) are required to reduce matrix effects (nebulizer, torch and sampling orifice blockage) as well as polyatomic ion interferences [164]. Chlorine-containing acids, such as HCl and HClO_4 , should not be used for acidification of samples because of the resulting formation of chlorine-containing polyatomic molecules which can produce signals overlapping with certain elements (e.g. As or Se). External calibration with an aqueous mixed element standard is normally sufficient for routine analysis [166]. Isotope dilution is a means of highly accurate analysis in both the single-element and multielement mode [71,83,167,168] which is essential in the analysis of

open ocean water [84]. ICP MS offers a rapid, convenient but not very precise method for the determination of isotopic ratios [84] (*cf.* Section 4.8.1). Better precision is obtained with ID TI MS [169,170]. ETV ICP MS has been proposed for ultratrace analysis of arctic snow [171].

Irradiation of water in sealed ampoules for neutron activation analysis is avoided because of radiolytic pressure build-up and the risk of explosion. Freeze drying is usually employed prior to radiation except when analysing for Hg (losses). Whereas the amount of residue from seawater is sufficient for an easy recovery of the freeze-dried salt, in the case of fresh waters a prior dissolution of a small amount of high purity substance, e.g. Na_2CO_3 is required. Alternatively, analytes can be concentrated on activated carbon or another sorbent which is then irradiated. A starting volume of 100 ml is usually employed. The most common interference is the Compton background from Na, Cl and Br that totally obscures the signals of the nuclides with comparable half-lives. In seawater Rb, Sr and Cs seem to be the only trace elements to be readily determined by INAA unless a pre-irradiation or radiochemical separation is used. In fresh waters the number of 15–20 elements which can be determined at normal levels by INAA can be doubled by radiochemical separation. As irradiation generally destroys metal-organic bonds speciation by NAA must be preceded by pre-irradiation separation, e.g. by gel electrophoresis [172]. The application of NAA to water analysis has been the subject of several papers [173–175] (*cf.* also Table 9.2).

X-ray fluorescence methods have widely been used for the direct analysis of water but the sensitivity is generally insufficient and thus preconcentration (usually by precipitation) is required [176,177]. Pre-oxidation with $\text{K}_2\text{S}_2\text{O}_8$ eliminated interferences from organic matter (low recoveries, long filtration times) [105]. Preconcentration and determination of trace elements in fresh water by means of functional filter paper containing fibres with chemically bonded chelate groups (commercially available) has been proposed [178]. Total reflection XRF offers sensitivities down to the ppb level by evaporation of small quantities (5–50 μl) onto very flat silica plates and high speed of multielement analysis [179–183]. The validity of evaporation for an improvement in the detection limits is restricted by the concentrations of alkali and alkaline earth elements. Also, some elements, e.g. S, K, Ca, tend to amplify matrix effects [68,89].

9.3 ROCKS, SOILS AND SEDIMENTS

Rocks are discussed in this book in the broad sense of the word including ores, placers, mattes and matte leach residues, concentrates and tailings which are usually analyzed in the prospecting for mineral reserves. The concentrations of dispersed trace elements in rocks are frequently employed by geochemists to examine the mineralogical, chemical and thermodynamic conditions that were present during rock formation. Less frequent needs are associated with the use of trace element patterns for tracing the provenance of archaeological artefacts and in geochronology (the determination of the age of rocks using naturally occurring radiogenic elements for which the abundance of one isotope slowly increases with time due to radioactive decay of a naturally occurring parent isotope). Requirements for geoanalysis have been discussed [184] with particular emphasis on automation [185,186]. Analysis of rocks has been the subject of an excellent monograph [187].

Soils are mixtures of mineral (sand and clay) and organic (humus and fulvic acids) materials. Soils consist of horizontal layers the upper of which are rich in organic materials whereas the lower have a composition similar to that of the parent rock. Analysis of soils has been reviewed [188–192].

Sediments have a similar matrix composition to soils. They occur suspended in still moving waters, or accumulated on the bottom of the hydrological system (river, lake, etc.). In general, suspended sediments are usually small-diameter particulates, easily mobilized and held in solution by hydrodynamic forces, while bottom sediments are larger-diameter higher-density particles that readily settle, or aggregates held together by chemical or physical forces. Sediments and soils are analyzed for exploration geochemistry and environmental purposes as they are the ultimate sink for the metal emissions. The most widely determined trace elements include Cu, Zn, Mn, Cr, Pb, Ni, Cd and V.

Wide-scale surveys imply the need for the analysis of a large number of samples for various elements in a cost-effective mode with reasonable (<5%) precision and accuracy. The two principal types of analysis include the analysis for total trace metals and analyses associated with various matrix components (speciation). The metals incorporated in the crystal lattice of quartz particles of soil and sediments are of no consequence to plant growth, food chains or drainage water chemistry and are seldom of concern. On the contrary, for rocks and related materials a complete chemical attack of the sample is required. Chemical separation

techniques are inadmissible on the grounds of cost with the exception of the analyses for rare and precious elements. Various analytical methods for geochemical exploration were discussed [193].

9.3.1 Sampling and physical sample preparation

Sediments are sampled using grab or core samplers depending on the type and quantity of sample required. The sampling of suspended sediments is best carried out using sediment traps. Grab samplers collect large volumes of samples, but often with considerable disturbance. Large, undisturbed samples are best collected with a box corer. Where depth profiling is of interest, sediment cores should be used. Metal devices should be modified with plastic liners to avoid sample contamination. Sampling of aquatic sediments in terms of design of a decision support system and a case study has been discussed [194].

Rock, soil and sediment samples are disaggregated and the particles greater than 2 mm are sieved out. The fraction below 2 mm is reduced to a fine powder to pass a 200 mesh (63 μm aperture) sieve by means of a swing-mill. Agate mortars are expensive but do not contaminate the sample with trace metals. A hard steel mortar is suitable if contamination with traces of steel constituents can be tolerated. Non-metallic sieves are recommended. Bauxites and ores of precious metals show remarkable grain size heterogeneities so precautions must be taken to avoid sampling errors [195]. Because of mineralogical heterogeneities of geological samples submilligram sampling is not recommended. For sediments a 20 μm size is usually chosen, but coarse silt (20–63 μm) and sand particle (>63 μm) fractions are sometimes also analyzed. Wet sieving is often preferable as it avoids the agglomeration which occurs on drying. Drying at 110°C is often practised, but losses of the more volatile elements (e.g. mercury) can occur. Dried sediments can be stored in plastic or glass containers. Moist sediments should be stored at 4°C or preferably frozen to prevent water losses.

9.3.2 Sample decomposition

In many rocks, almost the total concentration of a particular element may be contained in a single mineral, e.g. Zr in zircon, Cr in chromite or Sn in cassiterite, which can be extremely difficult to dissolve chemically. Minute grains that remain can be unnoticed leading to serious analytical errors [196]. Geological materials are usually decomposed by

fusion and/or dissolution in acids. Decomposition by fusion (*cf.* Section 2.2) is relatively rapid but losses of volatile elements, risk of contamination and the resulting high salt content are handicaps. Fusion with lithium borates followed by the dissolution of the melt has been discussed [197]. Automatic sample preparation for geosamples (weighing, fusion, dissolution, cation-exchange separation) has been discussed [185,186, 198–200] and applied to the analysis of oxidic ores [199] and various geochemical standards [200]. Acid dissolution often includes HCl–HNO₃ and HF usually in combination. Microwave-assisted decomposition is faster and should be given priority where possible [196]. Analysis for volatile elements and precious metals requires special approaches.

Silicate rocks include quartz (SiO₂), enstatite (MgSiO₃), beryl (Be₃Al₂Si₆O₁₈), kyanite (Al₂SiO₅), topaz [Al₂SiO₄(F,OH)₂], epidote [Ca₂(Al,Fe)₃(SiO₄)₃(OH)], and andradite [Ca₃Fe₂(SiO₄)₃]. Fusion with LiBO₂ [201] or LiBO₂–Li₂B₄O₇ (4+1) [202] was recommended for quick and complete dissolution of majority of silicates. Sodium carbonate fusions over standard Bunsen burners may suffer from an insufficient temperature to achieve a true fusion. The melt is dissolved in slightly warmed dilute HCl or HNO₃. An alternative approach is HF-based acid attack. For trace element analysis silicon needs to be removed as SiF₄ (losses of B, As, Ge, Sb can be expected). Otherwise silica gel, which traps the trace elements, precipitates [203]. Hydrofluoric acid is seldom used alone because of low solubility of KF and CaF₂ and because iron is left in an uncertain mixed state, but it is usually mixed with HClO₄ and HNO₃. Another method involves heating the samples with HNO₃–HClO₄ followed by a further treatment with HClO₄–HF [203]. Microwave-assisted pressure dissolution with a mixture of HF–*aqua regia* [204] or HNO₃–H₂O₂–HF [205] is gaining popularity. Many silicates contain about 80% quartz which is very resistant to acid attack, even by HF, but frequently the metals of interest can be quantitatively leached.

Phosphate rocks contain high levels of Ca and Si, so the use of HF to dissolve the Si may precipitate CaF₂. If the Ca content is very high (>50%) CaF₂ may not redissolve after addition of H₃BO₃. Precipitation of CaF₂ can be avoided by using HBF₄ instead of HF. Apatites are dissolved in 7 M HCl or HNO₃ [206]. Monazites ((Ce,La,Nd,Th)PO₄) and xenotime (YPO₄) are only negligibly attacked by a mixture of HCl and an oxidant. Sulphuric acid is the best of all mineral acids to open monacite with simple fuming.

Sulphate rocks include typically celestite (SrSO₄), anglesite (PbSO₄), anhydrite (CaSO₄) and barite (BaSO₄). Sulphates do not dissolve easily

in HCl although gypsum (CaSO_4) goes into solution on heating [206]. Celestite, anhydrite and anglesite were dissolved in boiling $\text{NH}_2\text{OH}-\text{HCl}-\text{HNO}_3$ [207]. Barite is highly resistant and requires an HClO_4 or H_2SO_4 attack.

Sulphide rocks consist of sulphides of Cu, Ni and Fe dispersed in silicate. Virtually all sulphides are decomposed by *aqua regia*. Sphalerite (ZnS), galena (PbS) and pyrrhotite ($\text{Fe}_{1-0.8}\text{S}$) are easily decomposed by boiling with 6–12 M HCl. Other sulphides: pyrite (FeS_2), chalcopyrite (CuFeS_2), molybdenite (MoS_2), cinnabar (HgS) are not attacked by HCl alone but are decomposed in the presence of an oxidant [208]. On heating the excess of the oxidant is removed. Pyrite, chalcopyrite and molybdenite are decomposed by hot 4 M HNO_3 . Oxidative attack (HNO_3 , *aqua regia*) is not suitable for galena as sparingly soluble PbSO_4 precipitates unless ammonium acetate is added [209]. Molybdenite ores and concentrates can be dissolved in $\text{HNO}_3-\text{H}_2\text{SO}_4$ but dissolution in HNO_3-Br is preferred with the oxidizing effect of the nascent Br_2 . Microwave-assisted pressure dissolution of sulphide mineral samples has been discussed [210]. Sulphide ores poor in silica can be decomposed by fusion with Na_2O_2 . The advantage of fusion over the acid digestion is that the sulphides are completely converted into sulphates, whereas acid digestion can result in the formation of a considerable amount of elemental sulphur [203]. Selenium and As can be quantitatively recovered only in ores decomposed in a pressure bomb (*cf.* Chapters 15 and 49).

Oxidic rocks may contain different compound forms of the elements depending on the geological type. The most important groups include iron ores, bauxites (hydrated aluminium oxides) and miscellaneous oxides of refractory metals. Oxides are generally soluble in halogen acids. The dissolving power increases with the complexing ability of the halogen with the metal. A chlorine-liberating solution of HCl and H_2O_2 was found to solubilize most of oxide minerals [208]. Various natural modifications of ferric oxide are slowly dissolved by HCl but the reaction is accelerated by SnCl_2 . Magnetite ($\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$) is readily dissolved in HCl or HBr. Natural iron arsenates ($2\text{FeAsO}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) dissolve completely in HCl [206]. Bauxites are poorly soluble in HCl because of poor solubility of AlCl_3 formed at the interface. Fusion with $\text{Na}_2\text{CO}_3-\text{Na}_2\text{B}_4\text{O}_7$ was recommended [195]. Tungsten ores (wolframite and scheelite (CaWO_4)) are dissolved in HCl and in *aqua regia* with possible formation of insoluble tungstic acid [206]. Uranium ores with small content of U(IV) are easily attacked by HCl. Uraninite requires an

oxidizing mixture of HCl with an oxidant, e.g. *aqua regia*. High percentage molybdenite ores and concentrates can be dissolved in a mixture of $\text{HNO}_3\text{--H}_2\text{SO}_4$. Chromite ($\text{Fe}^{\text{II}}\text{Cr}_2\text{O}_4$) is resistant to a boiling $\text{H}_2\text{SO}_4\text{--HF}$ mixture unless under pressure [211]. Fusion with Na_2O_2 in Ni crucibles is the most common approach. Nb–Ta ores are attacked by $\text{HNO}_3\text{--HF}$. A combination of H_2SO_4 decomposition with a final fusion of the residue with an alkali disulphate has been recommended for titanoniobates and -tantalates. Zirconia ZrO_2 , zircon ZrSiO_4 , niobite $(\text{FeMn})\text{O}\cdot\text{Nb}_2\text{O}_5$ and tantalite $(\text{FeMn})\cdot\text{Ta}_2\text{O}_5$ are very resistant minerals which require fusion rather than acid attack for total solubilization; fusion with LiBO_2 was found to be suitable [212].

Carbonate rocks including fluorocarbonates of REE, e.g. parisite $\{\text{Ca}(\text{La,Ce,...})[\text{F}_2(\text{CO}_3)_2]\}$, are soluble in HCl [206] or $\text{HCl--H}_2\text{O}_2$ [208]. Microwave digestion with HF--HNO_3 upon heating the sample with acetic acid to inhibit CaF_2 formation and H_3BO_3 addition to keep the silica in solution has been reported [213].

For *noble metal ores*, the decomposition technique is determined by the phase composition of the test material. Minerals containing Au (mostly pure nuggets or complex tellurides) are readily soluble in *aqua regia*. If As is present, the sample must be roasted to prevent the volatilization of Au probably as a low melting Au–As alloy (*cf.* Chapter 28). The platinum group metals are present in mineral raw materials as alloys, sulphides, tellurides and arsenides, mostly together with ores of Cu, Ni, Co, As and Fe. Many of them (e.g. sperrylite, cooperite, braggite) are not dissolved in *aqua regia* and must be roasted to be converted into soluble forms. The degree of *aqua regia* leaching is varied so the residue must be fused with Na_2O_2 . Chromite must be completely dissolved for quantitative recovery of the PGMs [214]. $\text{Na}_2\text{B}_4\text{O}_7\text{--Na}_2\text{CO}_3$ flux employing an NiS collector provides a very viscous inhomogeneous slag with chromite grains still present [214]. The improved method of chromite decomposition involving a two-step fusion with $\text{Li}_2\text{B}_4\text{O}_7\text{--Na}_2\text{CO}_3\text{--NaOH}$ and NiS collection has been reported [214]. Fire assay is a universal decomposition technique for precious metals ores (*cf.* Section 2.2.3). An alternative to acid digestion and fire assay is dry chlorination by passing hot Cl_2 gas over the sample either alone or containing NaCl to convert the metals in HCl soluble salts [215].

Well-defined particle size fractions from soils and sediments can be analyzed as slurries [216,217]. Partial digestion which may extract >90% of the analyte from the sample is usually a sufficient compromise between total recovery and the analysis time. For total decomposition

simple oxidizing acid digestions are used, rather than the more rigorous alkaline flux fusions. Pressure decomposition with HNO_3 [218–220] or $\text{HNO}_3\text{--HCl}$ [221–223] in Teflon bombs with or without microwave assistance is the most popular. Addition of HF is required [224–231]. For soils rich in organic matter H_2O_2 is added [232]. The Parr bomb technique is found to be preferred in acid digestion for multielement analysis by simultaneous ICP AES compared with microwave and hot plate methods for soils [237]. Microwave-assisted and conventional leaching for the determination of metals in soils, sediments, sludges have been discussed [233,235]. If fusion needs to be used, soils rich in organic matter or free iron-oxides should be predigested to minimize the risk of damage to Pt ware [234]. Recovery of trace metals from aquatic sediments by several procedures prior to FAAS has been discussed [236].

9.3.3 Determination techniques

The chemical composition of geomaterials is often complex and the matrix usually contains two or three major elements of almost equal concentration. Matrix interferences are common and should always be carefully considered. Plasma techniques (ICP AES and MS), reviewed for geochemical materials elsewhere [238], are the usual choice for routine analysis. Direct feeding of the solution obtained after the decomposition to the nebulizer is preferred for multielement analysis (Table 9.3). Separation and preconcentration are generally inadmissible for routine analysis but often used for customized analyses especially by AAS techniques (Table 9.4). Analysis for precious metals requires a deep knowledge of their chemistry; customized procedures are listed in Table 9.5. Procedures used for the analysis of soils and sediments for total element content are summarized in Table 9.6.

Flame AAS is satisfactory for Cu, Pb, Zn, Ni, Cd, Fe, Mn, Co, Ca and Mg. Precision for direct FAAS is 1–2% whereas the use of flow injection techniques leads to reproducibilities of 2–5% for high salt content solutions. The background interferences are corrected instrumentally while enhancement–suppression effects can be overcome by the method of standard additions. The performance of FAAS is enhanced by group extraction of trace elements as various complexes into MIBK followed by the determination directly in the organic phase [252,253] or on stripping the analytes with $\text{HNO}_3\text{--H}_2\text{O}_2$ [254,285]. Co-extraction of Fe is a common problem in solvent extraction. Iron(III) can be removed by

TABLE 9.3

Multielement trace analysis of geological materials after chemical decomposition without a separation/preconcentration step

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
CRMs (basalt, andesite)	fusion: $\text{Li}_2\text{B}_4\text{O}_7$	Ba, Be, Ce, Co, Cs, Cu, Eu, Ga, La, Lu, Mo, Sr, W, V, U, Yb, Zn	ICP MS	239
Bauxites (0.2 g)	fusion: Na_2CO_3 – $\text{Na}_2\text{B}_4\text{O}_7$	B, Ga, Mn, Ni, Sr, V, W	ICP AES	195
Sulphate rocks (0.1 g)	NH_2OH – HCl – HNO_3	40 elements	AAS, ICP AES, ICP MS	207
CRMs (rocks) (1 g)	H_2O_2 – HCl – HF	B, Ba, Be, Cd, Co, Cu, Li, Mn, Mo, Ni, Pb, Sc, Sr, V, Zn	ICP AES	206
Meteorites, CRM (rocks) (0.25 g)	<i>aqua regia</i> – HF (bomb)	Ba, Be, Cd, REE, Co, Cr, Cu, Li, Nb, Ni, Sc, Sr, Th, V, Y, Zn, Zr	ICP AES	240
CRMs (silicates) (0.1 g)	HNO_3 – HF – HClO_4	Ag, As, Ga, Rb, Sr, Mo, In, Sn, Sb, Te, Cs, Tl, Pb, Bi, Th, U	ICP MS	241
Sulphide minerals (1 g)	<i>aqua regia</i>	Ag, As, Bi, Cd, Co, Sb	FAAS	242
Limestone, granite, argillite (0.2 g)	HF , HNO_3 – HCl	Co, Cr, Cu, Mn, Ni, Pb, Zn	ICP AES GF AAS	243
Iron ores (0.1 g)	HNO_3 – HF – H_2O_2	40 elements	ICP MS	244
CRMs (silicate rocks)	HNO_3 – HF – HClO_4	REE	ICP MS	245
Rocks (0.1 g)	HNO_3 – HCl – HF (bomb)	REE	TXRF	246
Rocks (0.2 g)	HNO_3 – HClO_4 – HF	49 elements	ICP MS	247

TABLE 9.4

Multielement trace analysis of geological materials involving a separation/
preconcentration step

Sample (amount)	Decomposition	Preconcentration	Elements determined	Detection technique	Ref.
Silicate rocks (1 g)	HNO ₃ -HClO ₄ , HClO ₄ -HF	volatn. as hydrides	As, Sb, Se, Te	ICP AES	203
Sulphide ores (1 g)	fusion with Na ₂ O ₂	volatn. as hydrides	As, Sb, Se, Te	ICP AES	203
Stream sediments, CRM (lead concentrate) (1 g)	leaching with HNO ₃ -HCl	volatn. as hydrides	As, Bi, Sb, Se	FAAS	248
CRMs (sediments) (0.2 g)	HClO ₄ -HNO ₃ , HF-NO ₃	volatn. as hydrides	As, Bi, Sb	ICP AES	249
Quartz sand (2.5 g)	H ₂ SO ₄ -HF, HNO ₃	volatn. of matrix as SiF ₄	Ba, Ce, Co, Cr, Cu, La, Li, Mg, Mn, Mo, Rb, Sr, Th, U, W, Y, Zr	ICP MS	250
Rock, soil, stream sediment (2 g)	<i>aqua regia</i> , HF, HBr-Br ₂	extrn. as bromides (MIBK)	Au, In, Te, Tl	FAAS	251
CRMs (soils, sediments, rocks) (2 g)	<i>aqua regia</i> - Br ₂	extrn. as iodides with TOMA (MIBK)	Ag, Cd, Se, Te, Tl	FAAS GF AAS	252
Rocks	<i>aqua regia</i>	extrn. as iodides with TOMA (MIBK)	Ag, Cd, Se, Te, Tl	FAAS GF AAS	253
CRMs: Mo, W-Mo, Zn-Sn-Cu-Pb ores, silicates (1 g)	Br ₂ -HNO ₃ , H ₂ SO ₄ , HF, <i>aqua regia</i>	extrn. as iodides (MIBK), back-extrn. with HNO ₃ - H ₂ O ₂	Ag, Bi, Cd, Cu, In, Sb	FAAS	254

Sample (amount)	Decomposition	Preconcentration	Elements determined	Detection technique	Ref.
CRMs (sulphide, oxide, carbonate rocks) (1 g)	HCl-H ₂ O ₂	extrn. with Aliquat 336 (MIBK)	Ag, As, Bi, Cd, Cu, Pb, Mo, Sb, Zn	FAAS	208
Ores, concentrates and dust from copper metallurgy (1 g)	HCl-HNO ₃ (bomb)	extrn. of matrix as chlorides with Hex ₄ N ⁺ (MIBK)	Co, Cr, Mn, Ni	FAAS	255
CRMs (0.5 g)	fusion with LiBF ₄ , La ₂ O ₃ , H ₃ BO ₃	anion exchange	Cd, Co, Cu, Pb, Sn, Zn, Zr	ICP AES	256
CRMs (soil, sediments, rocks) (0.4 g)	fusion with LiBO ₂	pptn. with cupferron	Hf, Nb, Ta, Zr	ICP MS	212
CRMs (granites, basalt, bauxite, synthetic glass) (0.5 g)	fusion with Li ₂ B ₄ O ₇ -La ₂ O ₃ -H ₃ BO ₃	ion exchange on Dowex 1×10	Cd, Co, Cu, Pb, Sn, Zn, Zr	ICP AES	200

Extrn. = extraction; pptn. = precipitation; volatn. = volatilization.

extraction from HCl medium into MIBK leaving the analytes in the aqueous phase or reduced to Fe(II) by ascorbic acid to minimize its extraction into MIBK allowing for the isolation of the analytes [286].

Graphite furnace AAS is restricted to customized analysis for individual elements because of vulnerability to matrix interferences and the resulting low precision (10–20%). With direct solid sampling (a sample mixed with graphite powder), GF AAS can be used for trace determinations in rock samples when reference samples of the same geological family are available [287]. Rapid furnace programmes were used for the slurry (suspended in HF) GF AAS determination of Cr, Pb and Cu [288]. Slurry ETA AAS of silica-rich samples has been discussed [289]. Use of H₂ in slurry ETA AAS to decrease the background signal has been evaluated [290].

Inductively coupled plasma AES for the analysis of geological samples has been reviewed [291]. Slurry sampling is generally inappropriate despite long grinding because of particle size and segregation effects

TABLE 9.5

Multielement analysis of geological materials for noble metals

Sample (amount)	Decomposition	Separation and/or pre- concentration	Elements determined	Detection technique	Ref.
Pt ore (1–50 g)	lead fire assay	pptn. with formic acid	Ag, Au, Pd, Pt	FAAS	257
CRM (Pt ore) (20–30 g)	NiS fire assay	none	Au, Ir, Pd, Pt, Rh, Ru	ICP MS	258
CRMs (sand, basalt, silicates Pt ore) (25 g)	NiS fire assay	none	Au, Ir, Os, Pd, Pt, Rh, Ru	NAA	259
CRM ores (5 g)	NiS fire assay	none	Au, Ir, Os, Pd, Pt, Rh, Ru	ICP MS	260
Chromite (25 g)	NiS fire assay	none	Au, Ir, Os, Pd, Pt, Rh, Ru	NAA	214
SRM (Pt ore) (10 g)	NiS fire assay	none	Pd, Pt, Rh	GF AAS	261
Rocks (not specified)	NiS fire assay, dissoln. in HCl	none	Ir, Pd, Pt, Ru	ETV ICP MS	262
Rocks, ores (20–50 g)	NiS fire assay, dissoln. in HCl	copptn. with Te	Au, Ir, Pd, Pt, Rh	NAA	263
Silicates (5 g)	H ₂ SO ₄ –HF, fusion with Na ₂ O ₂	copptn. with Se/Te	Au, Pd, Pt, Rh	GF AAS	264
CRMs (sulphide ores) (2.5 g)	<i>aqua regia</i> , the residue fused with Na ₂ O ₂	SPE on dehydro- dithizone column	Au, Pd, Pt	DCP AES	265
Basic rocks and chromites (0.4–3 g)	HF–HClO ₄ – H ₂ SO ₄ (bomb)	ion-exchange with Lewatit- 207 or copptn. with Te or extrn. with N,N- diethyl-N'- benzoylthiourea	Au, Ir, Pd, Pt	GF AAS	211

Sample (amount)	Decomposition	Separation and/or pre- concentration	Elements determined	Detection technique	Ref.
Mn nodules, silicates (0.5–1.5 g)	HNO ₃ –HF (bomb)	copptn. with Se	Au, Ir, Os, Pd, Pt, Rh, Ru	GF AAS T XRF	266
Rocks (5 g)	HF– <i>aqua regia</i> (bomb)	anion exchange, Sarafion NMRR	Au, Ir, Pd, Pt, Rh	GF AAS	267
Minerals	HNO ₃ –HF (bomb)	SPE on poly (vinylthio- propionamide) chelating resin	Au, Ir, Pd, Pt	GF AAS	268
CRMs (Pt ore) (0.5 g)	HCl–HNO ₃	copptn. with Hg	Ag, Au, Pd, Pt, Rh	GF AAS	269
Rocks (2 g)	HNO ₃ –HCl	HPLC of MPTAE complexes	Ir, Os, Pd, Pt, Rh	VIS	270
Rocks (5 g)	HF– <i>aqua regia</i>	copptn. with Te	Pd, Pt, Rh, Ru	GF AAS	271
Rocks (5 g)	HF– <i>aqua regia</i>	cation exchange on Dowex 50W- X8	Ag, Au, Pd, Pt, Rh, Ru	GF AAS	271
Rocks, ores (≤50 g)	fluorination with XeF ₄ or ClF ₃	extrn. with N- octylaniline into MIBK, stripping into HClO ₄	Ir, Pd, Pt, Rh, Ru	GF AAS	272
Rocks (0.2–0.5 g)	fluorination with XeF ₄	trapping on CeF ₃ , selective volatn.	Ir, Os, Pd, Pt, Rh, Ru	AFS	273
CRM (Pt ore, rocks) (<25g)	dry chlorination	none	Au, Ir, Pd, Pt, Rh, Ru	ICP MS	215

Copptn. = coprecipitation; extrn. = extraction; pptn. = precipitation; volatn. = volatilization.

TABLE 9.6

Multielement trace analysis of soil and sediment for total metal content

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Marine sediments (0.3 g)	HCl-HNO ₃ , microwave assisted	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V, Zn	ICP AES, GF AAS (Cd), CV AAS (Hg)	221
CRM (marine sediments) (0.5 g)	HNO ₃ -HF-HClO ₄ (bomb)	Cd, Cr, Mo, Ni, Pb, Sb, Sn, Sr, Tl, U, Zn	ID ICP MS	167
Soils, sediments (0.5 g)	HNO ₃ (microwave assisted)	Ag, As, Ba, Cd, Cu, Cr, Hg, Ni, Pb, Se, Tl, Zn	GF AAS, CV AAS (Hg)	218
Soils, sediments (0.5–1 g)	<i>aqua regia</i> (microwave assisted)	Cd, Cr, Cu, Fe, Mn, Pb, Zn	FAAS, GF AAS, ICP AES	222
Sediments, soils (1–2 g)	HNO ₃ -HCl, residue refluxed in HCl	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Tl, V, Zn	FAAS, ICP AES	223
Sediments (0.2–1 g)	HNO ₃ /HF, <i>aqua regia</i>	Cd, Cr, Cu, Pb, Zn	ID MS ^a	224
CRMs (sediments, soils) (0.1–0.5 g)	HNO ₃ (microwave assisted)	Ag, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zn	ICP AES	219
Sediments (0.25 g)	HNO ₃ (microwave assisted)	Al, As, Ca, Cd, Cr, Cu, Fe, Ga, Hg, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn	TXRF	220
River sediments (0.05 g)	HNO ₃ -HClO ₄	Cd, Cr, Cu, Mn, Ni, Pb, Zn	AAS	274
Suspended matter (0.02 g)	HNO ₃ -HF	37 elements	TXRF	275
Sediments, suspended particulates (10 mg)	slurry in glycerol medium	Cd, Co, Cr, Cu, Ni, Pb	GF AAS	195
River sediment	slurry	As, Fe, Mn, Pb	GF AAS	217

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Marine sediment CRm (0.5 g)	<i>aqua regia</i> , HF– HCl, HClO ₄ –HNO ₃	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se.	GF AAS	276
Marine sediments (0.5 g)	HF–HNO ₃ –HClO ₄	Cd, Cr, Mo, Ni, Pb, Sb, Sn, Sr, Tl, U, Zn	ID ICP MS	277
Marine sediments (0.5 g)	HNO ₃ –HF–HClO ₄	As, Cd, Co, Cu, Mn, Mo, Ni, Pb, V, Zn	ICP MS	225
CRMs (sediments) (0.25 g)	HNO ₃ –HF–HClO ₄ (bomb)	As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn	GF AAS	226
CRMs (soils) (0.5)	leaching with CH ₃ COONH ₄ , CH ₃ COOH, EDTA	As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Ti, V, Zn	ICP AES	278
CRMs (soils, sediments) (1 g)	HF–HNO ₃ (bomb), HF–H ₂ SO ₄	Ag, B, Ba, Be, Cd, Co, Cu, Li, Mo, Na, Ni, Sn, Zn	ICP AES	227
CRMs (soils, sediments) (1 g)	HF–HNO ₃ (bomb), HF–H ₂ SO ₄	B, Be, Co, Mo, Sn	ICP AES	228
Soil	HF–HNO ₃ (bomb), HF–H ₂ SO ₄	B, Be, Co, Mo, Sn	ICP AES	279
Soils (0.25 g)	fusion with LiBO ₂	Al, Ba, Mn, Si, Ti, V, Y, Zr	ICP MS	234
Soils, sediments (0.25 g)	HNO ₃ –HF–HClO ₄ (bomb)	As, Cd, Cr, Mn, Mo, Pb, Sb	ICP MS	229
Soils, sediments (0.5 g)	HNO ₃ , HF, HClO ₄	Co, Cr, Cu, Mg, Mn, Ni, Pb, Sr, Ti, V, Zn, Zr	ICP AES	230
Soils, sediments (1 g)	HF–HNO ₃ –HClO ₄ , pptn. with HMA HMDTC	Ag, Bi, Cd, Co, Cu, Hg, In, Mo, Ni, Pb, Se, Zn	FAAS, XRF	231
Marine sediment (0.25 g)	HNO ₃ –HF (vapour phase)	As, Cd, Co, Cr, Cu, Mn*, Ni, Pb, Sn, V, Zn*	GF AAS* FAAS	280
Sediments	HNO ₃ (bomb)	Cd, Cu, Fe, Pb, Zn	AAS	227

(continued)

TABLE 9.6 (continuation)

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Sediments	HNO ₃ -HF	Cd, Cu, Cr, Pb, Zn	ID TI MS ^a	281
CRMs (fly ash, soil, sediments) (1 g)	HF-HNO ₃ , HClO ₄ (bomb)	Cd, Cu, Pb	FI FAAS ^a	282
CRM (soils, sediments) (0.1-0.2 g)	HNO ₃ -H ₂ O ₂ -HF (bomb, microwave assisted)	Ba, Cr, Cu, Mn, Sr, Zn	ICP AES	283
CRMs (soils, sediments) (1 g)	Br ₂ , HNO ₃ , HF, HClO ₄ , HCl, extrn. with ethyl xanthate (CHCl ₃)	Bi, Co, In, Ni, Pb	FAAS	284

a After separation-preconcentration; pptn. = precipitation; extrn. = extraction.

during transportation to plasma [252,292,293]. Hydride generation ICP AES is the common method for the determination of Hg, As, Sb, Bi, Se and Te [203]. Sorption or ion exchange is used for the separation of the matrix [200]. The use of multiple internal standards for calibration in routine analysis has been discussed [294]. Non-linear spectral interferences for simultaneous ICP AES of soil samples have been evaluated [295].

Inductively coupled plasma MS allows for the simultaneous determination of both elemental concentrations and isotope ratios. Applications in geological trace analysis were reviewed [296]. Application of ICP MS to environmental analysis was discussed (soil, dust) [297]. Polyatomic ion interferences (*cf.* Section 4.8.1) generated from the sample itself or from the medium used for sample dissolution pose a serious problem in ICP MS analysis of geochemical samples. Fusion methods and chlorine-containing acids should be avoided; nitric acid is preferred. Flow injection ICP MS has been used for samples after Li₂B₄O₇ fusion [239,298]. ICP MS is particularly useful for the REE and PGM determinations and for the analysis of samples rich in Ca, Mn and Fe (e.g. nodules or limestones) which are affected in AAS and AES by high background and complex matrix spectra. The determination of precious metals in geological samples by ICP MS has been reviewed [299]. ICP MS gains popularity in geochronology since it is faster than ID TI MS.

X-ray fluorescence is the most widely used instrumental method of analyzing rock samples for the major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) and selected trace elements including Rb, Sr, Y, Nb, Zr, Cr, Ni, Cu, Zn, Ge, Ba, Pb and U (*cf.* Section 4.6.3). Detection limits for many of them lie in the range 1–10 ppm under routine operating conditions.

Neutron activation analysis has still retained significance for the certification of reference materials. Instrumental NAA has been discussed [300–302]. Results obtained for 12 elements by INAA were compared with those obtained by ICP AES, XRF and AAS; the elements Na, Fe, Ba, Co, Cr, La, Ni and Rb could be determined in rocks by INAA with sufficient sensitivity and precision whereas the determination of Ag, Yb, Zn and Zr suffered from inadequate sensitivity [303]. Nuclear methods for elemental analysis of sediments were discussed [303a].

9.4 ASHES, SLAGS AND SOLID WASTES

Combustion of coal and incineration of municipal wastes produce considerable amounts of light ash (fly ash) and heavier bottom ash or slag. Their analysis for trace and minor elements is important for the evaluation of the release of heavy metals *via* volatilization or leaching. Samples are usually ground (or disaggregated), homogenized prior to analysis and sieved. Because of the multicomponent nature of the slag material preferential size reduction depending on the hardness of each mineral may occur [304]. Bulk analysis is the most popular but the surface adsorbed fraction is essential as it is subject to leaching [305]. Analysis of particle fractions is sometimes done [306].

Ash and slag samples are often difficult to dissolve so direct techniques (INAA [306,325], XRF [306,307]) are preferred. To assess the environmental impact leaching with water [306], acetic acid [308] or H_2SO_4 [309] or partial microwave-assisted digestion with HNO_3 [310] or HNO_3 -2-ethylhexan-1-ol [310,311] are fully sufficient. For total content monitoring, direct multielement analysis on spark ablation of pressed pellet [312] or slurry introduction [304] have been reported. For dissolution, acid digestion, almost uniquely in pressure bombs and preferably microwave assisted, is favoured over fusion. The use of HNO_3 alone has been widely reported [308,310,313,314] but silicate residues are likely to remain which requires addition of HF. On the other hand HF alone fails for materials rich in Fe, Ca or P [315] and

leads to insoluble Al, Ca, K and Na fluoride residues [316]. Complexation with H_3BO_3 has been used to remove excess of fluoride after HF decomposition [315–318]. The mixtures HNO_3 –HF [318–320], HNO_3 –HF– HClO_4 [317] and HNO_3 – H_2O_2 [321] have been used. Fusion with $\text{Li}_2\text{B}_4\text{O}_7$ and subsequent dissolution with HClO_4 or HCl [322] is less suitable because it is cumbersome and a high salt load is introduced. Various methods have been compared [316,321,322]. Leachability of toxic elements (Cd, As, Hg, Se) from solid wastes has been examined [323]. Six digestion methods for solid wastes (sewage sludge with organic coagulant, sewage sludge with inorganic coagulant, a compost of pig waste with sawdust) were compared and HNO_3 – HClO_4 –HF was found to be the most suitable for the determination of Be, V, Ga, Sb, La and Bi by means of ICP MS [324].

Separation procedures are seldom applied in the analysis of ashes and solid wastes. Interference for alkali and alkaline earth metals with ED XRF of fly ash was removed by reverse-phase chromatography or solvent extraction of DDTC complexes [307]. Flame AAS for higher concentration levels is fully sufficient [310,311,326] but ICP AES is definitely the most popular technique owing to spectrally simple aluminosilicate matrix. Selected analytical procedures for multielement analysis of solid wastes are summarized in Table 9.7.

9.5 SPECIATION

9.5.1 Water

Specific requirements for sampling prior to speciation analysis have been discussed [332]. Most of the V, Fe, Co, Cu, Cd in seawater exists as complexes with large biological molecules [333]. In fresh waters heavy metals occur complexed with humic substances [334]. The removal of one or more species from the matrix should not disturb the solution equilibria. This seldom occurs and operationally defined separation techniques are used to compare different samples [332,335,336]. They include size–mass fractionation techniques (filtration, ultrafiltration, centrifugation, field flow fractionation) [337], extraction and sorption techniques. Extraction with octanol or hexane–10% butanol is used to measure the lipid-soluble fraction of a metal in water [338]. Complexation of metals with humic and fulvic acids has been discussed [334,339,340]. Multielement speciation of trace transition metals in

TABLE 9.7

Multielement trace analysis of ashes, slags and solid wastes

Sample (amount)	Digestion	Elements determined	Detn. technique	Ref.
CRMs (0.1–0.2 g)	HF– <i>aqua regia</i> (microwave assisted)	Ba, Co, Cr, Cu, Co, Fe, Mn, Ni, Sc, Ti, V, Zn	ICP AES	322
Copper plant fly ash	HCl–HNO ₃ –HF (microwave assisted)	Ba, Cd, Ce, Co, Cr, Cs, Li, Mn, Mo, Ni, Rb, Sr, Ti, V, Zr	ICP AES	318
CRMs (0.1–0.2 g)	fusion with Li ₂ B ₄ O ₇ , dissoln. in HCl	Ba, Co, Cr, Cu, Fe, Mn, Ni, Sc, V, Zn, Zr	ICP AES	322
CRMs (0.1–0.2 g)	HF– <i>aqua regia</i> (bomb)	Ba, Co, Cr, Cu, Fe, Mn, Ni, Sc, Ti, V, Zn	ICP AES	322
Solid waste (1–2 g)	HNO ₃ –H ₂ O ₂ , refluxing of the digestate with HNO ₃ or HCl	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn	ICP AES	321
Sewage sludge (1 g)	HNO ₃ –HF (bomb), open vessel HF–H ₂ SO ₄	Ag, B, Ba, Be, Cd, Co, Cu, Li, Mo, Ni, Sn, Zn	ICP AES	320
Sewage sludge (1 g)	HNO ₃ –HF (bomb), open vessel HF–H ₂ SO ₄	B, Be, Co, Mo, Sn	ICP AES	319
Sewage sludge	HNO ₃ (bomb)	Cd, Cr, Cu, Pb, Ni, Zn	ICP AES	314
Solid waste (0.1–0.5 g)	HNO ₃ (microwave assisted)	Ag, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zn	ICP AES	313
Sewage sludge (0.5 g)	HNO ₃ –2-ethylhexan-1- ol (microwave assisted)	Cd, Cu, Fe, Mn, Pb, Zn	FAAS	311
Solid waste (1–2 g)	HNO ₃ –HCl, residue refluxed in HCl	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Tl, V, Zn	FAAS ICP AES	327

continued

TABLE 9.7 (continuation)

Sample (amount)	Digestion	Elements determined	Detn. technique	Ref.
Solid urban waste	HNO ₃ (bomb)	As, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	ICP AES	308
City waste incinerator ash (1 g)	HNO ₃ -HF (bomb)	Ba, Cd, Cr, Fe, Ni, Pb, Sb, K, La, Mn, Ti, V, Zn	ICP AES	316
City waste incinerator ash (1 g)	fusion with Li ₂ B ₄ O ₇ , dissoln. in HClO ₄	Ba, Cd, Cr, Fe, Ni, Pb, Sb, K, La, Mn, Ti, V, Zn	ICP AES	316
Copper plant fly ash	fusion with Li ₂ B ₄ O ₇ , dissoln. in HNO ₃	Ba, Cd, Ce, Co, Cr, Cs, Li, Mn, Mo, Ni, Rb, Sr, Ti, V, Zr	ICP AES	318
City waste incinerator ash and slag (1 g)	HNO ₃ -HF (bomb)	Ag, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Sr, Ti, V, Y, Zn, Zr	ICP AES	306
Sewage sludge	HNO ₃ (microwave assisted)	Cu, Mn, Pb	slurry FI FAAS	310
Coal ash (50 mg)	HF	Fe, Ti, Mn, K	ICP AES	315
Electric furnace dust, 0.5 g	fusion with Li ₂ B ₄ O ₇ - La ₂ O ₃ -H ₃ BO ₃	Cd, Cu, Pb, Zn	ICP AES ^a	328
Fly ash (0.1 g)	HF, H ₂ SO ₄ -HNO ₃ (bomb) or Li ₂ B ₄ O ₇ - LiBO ₂ fusion	Be, Fe, Mg, Ti, Mn, Be	GF AAS	329

^a After ion-exchange on Dowex 1×10.

fresh water, which is based on their fractionation on three sorbents, Chelex-100, Sep-Pak C18 and Fractogel DEAE, and distinguishes between labile complexes, non-polar organic adsorbable matter and ion-exchangeable substances, has been developed [120]. In another speciation scheme for river water Amberlite XAD-2 pretreated with In³⁺

to saturate cation exchange sites was used for selective sorption of humic and fulvic complexes of Cd, Cu, Pb at pH 5. Inorganic cations and anions, EDTA complexes and colloidal hydrated Fe(III) were not retained [340]. Co-electrodeposition with mercury on pyrolytic graphite platforms was proposed for GF AAS determination of labile lead in saline (sea and estuarine) waters [341]. The advanced hyphenated techniques for speciation of particular elements are described in Part III.

9.5.2 Sediments and soils

For speciation analysis sediments should be handled in an inert atmosphere to avoid oxidation. Sampling and storage for speciation analysis have been reviewed [332]. Leaching to liberate metals from less resistant minerals such as clays, hydrolyzates (Fe and Mn oxides) or organic matter is usually completely satisfactory to evaluate the bioavailability of trace elements and hence their toxicity. A selective extractant might be chosen which will attack a specific component of the soil and release the trace elements therein. Extractants selective to a given organic compound are generally not available so operational approaches are in use. The extractants include solutions of acids, ligands capable of reversing chemisorption equilibria (e.g., EDTA, DTPA, TEA), and simple salts to displace loosely bound metal ions bound to ion exchange sites on clay minerals.

Acid-extractable metals are defined as those loosely bound, absorbed or precipitated on grain surfaces. This is a reliable method only if a number of samples are compared. They represent 60–95% of the total depending on the metal and sample. Dilute rather than concentrated HNO_3 and HCl result in higher recovery rates [221]. A careful choice of leaching agents makes sequential element speciation possible (*cf.* Table 9.8). The fractions are operationally defined, e.g. (i) water soluble (H_2O), (ii) easily exchangeable (BaCl_2 , MgCl_2 , ammonium acetate), (iii) strongly adsorbed (e.g. EDTA), (iv) secondary clay minerals and metal oxides (dilute HCl , HNO_3), (v) organically bound (hexane extractable, released under oxidizing conditions) and (vi) primary minerals or highly fixed ions. Some individual examples are given in chapters devoted to individual elements (Cu, Zn, Pb). Other methods for speciation such as equilibration with ion exchanger [345,347] or chromatography fractionation of the leachates are less popular. Operational methods for speciation analysis of sediments and soil are summarized in Table 9.8. Methods for determining the different forms of metals in sediments

TABLE 9.8

Speciation of trace elements in sediments and soils

Sample (amount)	Leaching agents	Analytes	Detection technique	Ref.
Polluted soils	I: water. II: BaCl ₂ III: acetate buffer/EDTA IV: HNO ₃	Cd, Cu, Pb, Zn	ICP AES	342
Sediments (200 mg)	microwave assisted: I: 1 M MgCl ₂ . II: 1 M acetate buffer, pH 5. III: 0.04 M NH ₂ OH.HCl in acetate buffer. IV: 0.02 M HNO ₃ -30% H ₂ O ₂ , pH 2. V: HNO ₃ -HCl	Cr, Fe, Mn, Pb, Zn	FAAS	343
Sediments	I: CH ₃ COONH ₄ soln., pH 4.5 II: CH ₃ COONH ₄ /EDTA, pH 5.5 III: CH ₃ COONH ₄ /EDTA, pH 3.5 IV: ammonium oxalate, pH 3.0 V: 7.25 M HNO ₃ . VI: 6 M HCl VII: <i>aqua regia</i>	Al, As, Cr, Cu, Co, Fe, Mn, Ni, Pb, Zn	FAAS, GF AAS	344
Sediments (0.5 g)	equilibration with ion exchanger, extrn. from the resin with EDTA soln.	Cd, Cu, Pb, Zn	FAAS	345
Sediments (1 g)	I: water. II: 1 M MgCl ₂ III: CH ₃ COONa, pH 5 IV: 0.04 M NH ₂ OH.HCl in CH ₃ COOH V: HNO ₃ -H ₂ O ₂	Cd, Cu, Fe, Mn, Pb, Zn	FAAS	346
Soil (5.0 g)	equilibration with ion exchanger, extrn. from the resin with NH ₄ Cl	Ca, Mg, Na, K	ICP AES	347
Soils (5 g)	I: 1 M MgCl ₂ . II: CH ₃ COONa, pH 5. III: 0.04 M NH ₂ OH.HCl in CH ₃ COOH. IV: 0.02 M HNO ₃ -30% H ₂ O ₂ . V: HF-HClO ₄	Cd, Co, Cu, Fe, Li, Mn, Ni, Pb, Zn	FAAS	348
Soils (0.5 g)	I: 1 M MgCl ₂ . II: CH ₃ COONa, pH 5. III: 0.04 M NH ₂ OH.HCl in CH ₃ COOH. IV: 0.02 M HNO ₃ -30% H ₂ O ₂ . V: HF-HClO ₄	Ag, Sb	INAA	348

Sample (amount)	Leaching agents	Analytes	Detection technique	Ref.
Model soil	I: 1 M MgCl_2 (pH 7) II: 1 M CH_3COONa (pH 5) III: 0.04 M $\text{NH}_2\text{OH.HCl}$ in CH_3COOH IV: 0.02 M HNO_3 –30% H_2O_2 V: HF – <i>aqua regia</i> (bomb)	Al, Ca, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, Zn	ICP AES	350
River sediment	I: CH_3COOH . II: $\text{NH}_2\text{OH.HCl}$ III: $\text{CH}_3\text{COONH}_4$ followed by H_2O_2	Cd, Cr, Cu, Ni, Pb, Zn	FAAS	351
Coastal sediments	I: water. II: $\text{CH}_3\text{COONH}_4$ (pH 7) III: $\text{CH}_3\text{COONH}_4$ (pH 5). IV: H_2O_2 V: $\text{NH}_2\text{OH.HCl}$. VI: HF	Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Ti, V	ICP AES	349

include sequential extraction, whereby a series of single reagents is used to extract operationally defined phases from the sediment in a defined sequence [351]. Single and sequential extractions in sediments and soils have been critically discussed [352].

9.6 QUALITY CONTROL AND ASSURANCE

9.6.1 Contamination

It is strongly advised to perform loading and unloading of filters used for collection of particulates in a laminar flow clean bench. Contamination control in atmospheric trace element research has been discussed in detail [353] with emphasis on ultraclean sampling of polar samples [354]. Contamination risk is also the most critical issue in water analysis owing to the large samples handled and low concentrations involved. Clean room condition of class 100 are essential [71,81,86,89,101]. Pre-concentration resins should usually be purified [117,84] and prepurified reagents should be used [81]. Polypropylene tips instead of coloured Eppendorf tips should be used [117]. Alkalis should be avoided as they

contain Ni whereas a Ga collector was found to be contaminated by Cr [99]. The pH-meter probe was found to be a significant source of contamination [84]. Polyethylene bottles were found to release Ni, new bottles cleaned with HNO_3 were recommended [84]. Cleaning and conditioning are essential both to reduce contamination risk and to minimize the potential losses by adsorption onto the container walls. In general, soaking in dilute acids is sufficient to remove surface metal impurities; however, it is possible that this may activate adsorption sites.

9.6.2 Losses

For aerosol samples, some elements may be volatilized as a result of chemical reactions which take place during the sample storage. Such losses may be minimized by storing the samples in a cool, dark place, preferably in a freezer. The viability of filter samplers for the collection of airborne particulates containing high vapour pressure compounds is open to doubt as conditions at the filter surface favour desorption or volatilization.

9.6.3 Reference materials

Accuracy is still a problematic issue owing to the lack of certified reference materials for fairly pure aerosols. Gaseous standards containing particulates of known composition and particle size distribution are not available. A way of circumventing this problem by using a suspension of a certified fly ash in an aqueous cellulose solution has been proposed. Their analyses may not cover for losses associated with adsorption during storage and unknown speciation as the matrix is almost never sufficiently matched. Preparation of an ambient aerosol filter reference material for elemental analysis has been described [282]. The wide range of certified reference materials available for environmental materials is summarized in Table 9.9. There exist hundreds of reference materials to be used in geological analysis. A comprehensive list of geological CRMs available can be found elsewhere [355]. Update information can be obtained from any national reference materials agency (*cf.* Section 8.4). The necessity for the development of reference materials for speciation analysis of sediments and soils has been emphasized and the activity of BCR in this field has been presented [356]. Stability of extractable trace metal contents in a river sediment has been studied using sequential extraction [357].

TABLE 9.9

Certified reference materials (CRMs) for environmental materials

Material	Description	Elements with certified content
NRCC CASS 3	coastal seawater	As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se(IV), Se(total), Zn, U
NRCC NASS 4	open seawater	As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, Zn
NRCC SLEW 2	estuarine water	As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn
NRCC SLRS 3	river water	Al, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sb, V, Zn
BCR CRM 505	estuarine water	Cd, Cu, Ni, Zn
BCR CRM 403	seawater	Cd, Cu, Mo, Ni, Pb, Zn
NIST SRM 1643c	Water	Ag, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Sr, Tl, V, Zn
NIST SRM 1633a	coal fly ash	Al, As, Cd, Ca, Cr, Cu, Fe, Hg, Mg, Mn, Ni, K, Pb, Rb, Se, Sb, Si, Na, Sr, Tl, Th, U, V, Zn
NIST SRM 1648	urban particulate matter	Al, As, Cd, Cr, Fe, Pb, Ni, K, Na, Se, U, V, Zn
NIST SRM 2689	coal fly ash low lime	Al, Ca, Fe, Mg, P, K, Si, Na, Ti
NIST SRM 2690	coal fly ash medium lime	Al, Ca, Fe, Mg, P, K, Si, Na, Ti
NIST SRM 2691	coal fly ash high lime	Al, Ca, Fe, Mg, P, K, Si, Na, Ti
BCR CRM 038	fly ash from pulverised coal	As, Cd, Co, Cu, Fe, Hg, Mn, Pb, Zn, Na
BCR CRM 176	city waste incineration ash	Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Tl, Zn
BCR CRM 145R	sewage sludge	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
BCR CRM 146	sewage sludge of mainly industrial origin	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
NIES8	vehicle exhaust particulates	Al, As, Cd, Ca, Cr, Co, Cu, Pb, Mg, Ni, K, Na, Sb, Sr, V, Zn
NIST SRM 2704	Buffalo River sediment	Al, As, Ba, Cd, Ca, C, Cr, Co, Cu, Fe, Mg, Mn, Pb, Hg, Ni, K, Si, Na, Sb, Tl, Ti, U, V, Zn
NIST SRM 1646	estuarine sediment	Al, As, Cd, Ca, Cr, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, V, Zn
BCR CRM 277	estuarine sediment	As, Cd, Cr, Cu, Hg, Ni, Pb, Sc, Se, Zn
BCR CRM 320	river sediment	As, Cd, Cr, Cu, Hg, Ni, Pb, Sc, Se, Zn
BCR CRM 141	calcareous loam soil	Cd, Cu, Hg, Pb, Zn
BCR CRM 142	light sandy soil	Cd, Co, Cu, Mn, Ni, Pb
BCR CRM 143	sewage sludge amended soil	Cd, Co, Cu, Hg, Mn, Ni, Zn

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Biological and clinical materials

These samples are very diverse and can be divided into biomedical materials (human tissues and excreta), ecological materials (plant and animal tissues) and foodstuffs. They are characterized by an organic matrix and percent or sub-percent concentrations of Na, K, Ca, Mg and Si with Cl^- , PO_4^{3-} , or SO_4^{2-} as counterions. Trace elements are usually determined for the purpose of clinical and environmental toxicology and nutrition. The state of the art, trends and demands on trace element analysis in biological matrices have been critically discussed [1–7]. This chapter describes pretreatment of different biological materials and approaches to multielement analysis. Determination of particular elements is discussed in Part III.

10.1 GENERAL CONSIDERATIONS

10.1.1 Sampling and storage

Meaningful data can only be obtained by close collaboration of the analyst with clinicians and toxicologists. For representative sampling several grams of solid material needs to be taken and homogenized to reduce the effect of sample heterogeneity to an acceptable level. Biological samples are often stored frozen. Thawing should be done slowly without heat and in a closed container to prevent moisture loss by drying or gain by condensation. The contamination hazard should be evaluated with respect to the sample analyzed and the element(s) determined. Analytical aspects of sample collection, storage and treatment have been reviewed [8–10].

10.1.2 Direct analysis

Direct analysis using the slurry technique (*cf.* Section 4.2.3) is gaining popularity, especially for plants and foodstuffs [11]. With ICP MS detection limits from 0.1 ng g^{-1} for U to $0.5 \text{ } \mu\text{g g}^{-1}$ for Zn can be obtained [12]. Instrumental NAA is affected by high concentrations of easily activated Na, P, Cl and Br and fails for many important nuclides (*cf.* Section 4.7.1). Laser ablation ICP MS is a promising tool for rapid multielement screening of pressed pellets but is hampered by sample inhomogeneity and calibration problems [13].

10.1.3 Digestion

Several biologically important elements (e.g. As, Hg, Sb, Se) are subject to losses during drying or ashing, but can be recovered reliably if wet ashing is performed in a PTFE bomb [14] (*cf.* Section 2.1.3). A $\text{HNO}_3\text{--H}_2\text{O}_2$ mixture is the first choice but the presence of HClO_4 and H_2SO_4 may be necessary to complete the attack. For fat and lipid containing materials combination of dry and wet ashing [15] or carbonization (heating at 300°C for 1–2 h) is recommended [16] but losses of volatile elements cannot be avoided. Microwave-assisted digestion shortens the analysis time considerably and is absolutely preferred [17,18]; a convenient way to perform it in an AAS sample cup has been proposed [19]. Open-vessel digestion is discouraged for ultratrace elemental analysis. Acid–vapour phase pressure decomposition with HNO_3 is a clean approach [20].

10.1.4 Separation and/or preconcentration

Ion chromatography using chelating resins was proposed for removal of alkali and alkaline earth metals and preconcentration of transition metals [21–23]. Alternative approaches include precipitation of Cd, Cu, Co, Pb, Mo and Ni with APDC [24–26] or extraction with APDC [27] following the complete digestion. These approaches are contamination prone and fail for ultratrace analysis unless by RNAA [28].

10.1.5 Determination

Factors influencing the reliability of FAAS determination of trace and minor elements (Cu, Mn, Zn, Fe) in biological materials have been

discussed [29]. GF AAS is a method preferably employed for the determination of most of the trace elements in biotic matrices. Solid samples are readily analyzed especially for elements with unproblematic chemical behaviour during atomization (e.g. for Cd, Zn, Cu, Sb) [2]. The non-specific absorption is removed by a careful optimization of the heating program and Zeeman background correction. Organic constituents are volatilized at 600°C whereas NaCl and KCl are selectively volatilized at above 1000°C. A common remedy is to add NH_4NO_3 and to volatilize chloride as NH_4Cl . Refractory oxides (CaO , MgO , Al_2O_3) can interfere severely with the determination of high boiling point metals. The application of ICP AES has been discussed [30,31]. Inductively coupled plasma MS offers unmatched advantages in terms of multielement analysis, high sensitivity and possibility of isotopic ratio determination and is a unique technique for studies of mineral metabolism based on stable isotope tracer concepts [32,33]. The use of several internal standards covering the same mass range as the elements to be determined with linear interpolation between internal standards provided effective correction for drift and matrix effects [34]. Signal suppression due to the salt content is easily overcome by dilution [35]. Applications of ICP MS in analysis of biosamples have been reviewed [36–38]. Neutron activation analysis has been playing an important role in the certification of reference materials because of relative freedom of contamination, but it cannot be applied to routine analysis [39,40].

10.1.6 Microanalysis

Microanalysis, e.g. of liver mitochondria [41] or individual specimens [42], is enjoying increasing interest. Rapid freezing of samples to avoid the ion movement between sub-cellular units encountered with homogenization and fractionation of tissue [41] and microdigestion procedures [42] are required.

10.2 BIOMEDICAL MATERIALS

These include human body fluids, soft and hard tissues. Blood, tissue and organ samples are analyzed for trace elements to detect abnormalities which may be due to a clinical problem. Traces of Cu, Fe, Pb, Rb, Sr, Zn occur in concentrations above $1 \mu\text{g g}^{-1}$ whereas those of Al, Au, Ba, Cd, Co, Cr, Cs, Mn, Mo, Ni and Sn are below $1 \mu\text{g g}^{-1}$ but above $0.01 \mu\text{g g}^{-1}$. The remaining elements are present at ultratrace concentration

in the body, below $0.01 \mu\text{g g}^{-1}$. Reference values of trace elements in human clinical specimens have been summarized [3,43].

Sampling and storage

In the biomedical field, in addition to many non-chemical factors, such as post-mortem changes, effects of medication, genetic factors and representativeness [44,45], contamination control is the crucial part of analysis and a common source of errors. Technical consideration for sample collection, storage, and treatment of samples for trace element analysis have been discussed [8,9,46–48]. Sample containers represent one of the earliest and potentially the largest sources of contamination (*cf.* Section 8.2). Another source are surgical instruments (needles for venipuncture, blades for sampling soft tissue, scissors for nails or hair) always needed except when sampling sweat, saliva, urine or faeces. For many elements (e.g. As, Cd, Co, Cr, Mn, Mo, Ni, Pb, Sb and V) sufficient contamination control can only be achieved by the use of special tools and reagents and by working in a controlled (dust-free) environment. Minimization of blank values in NAA analysis of biological samples considering the whole procedure has been discussed [49].

Determination

Analytical techniques for the analysis of biomedical (clinical) samples were reviewed [50] with particular emphasis on GF AAS [51–54], ICP AES [30,55,56], fluorometry [57] and NAA [58–60]. Polyatomic interferences in ICP MS analysis were discussed [61].

10.2.1 Body fluids

These include blood and serum, urine, milk and less-often analyzed amniotic and cerebrospinal fluids, sperm, and gastric and pancreatic juices. Whole blood has in practice no significance for diagnosis or for therapy control using the trace element status, with the exception of Cd and Pb which bind to the erythrocytes. Serum normal levels of many elements of high potential interest are very low which makes their accurate determination a challenging task [3,43]. The trace elements in serum are mostly bound to proteins and therefore their concentrations should be standardized to the total protein content. Urine and faeces are usually analyzed for industrial health reasons. Procedures developed in recent years and involving a chemical pretreatment step are given in Table 10.1.

TABLE 10.1

Multielement trace analysis of body fluids

Sample (amount)	Dissolution	Elements determined	Detection technique	Ref.
Blood	HNO ₃ , HClO ₄ (bomb)	As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Se, Si, Sr, Zn	ICP AES	62
Blood, serum (1 ml)	HNO ₃ (microwave assisted)	Mn, Ni, Pb	TXRF ¹	63
Blood and milk	copptn. with Bi(PDC) ₃ or Ni(PDC) ₂	Cd, Co, Cr, Fe, Mo, Ni, Se, Ti, V, Zn	RNAA	64
Serum	diln. with 1% HNO ₃	Co, Cs, Cu, Fe, Mo, Rb, Zn	ICP MS	65, 66
Serum (2 ml)	dry ashing [Mg(NO ₃) ₂]	Al, Co, Mn, Mo, Ni, V	AAS	67
Serum CRM		Cr, Cu, Pb	ICP MS	68
Serum	diln. with matrix modifier	Al, Cr, Cu, Mn, Se, Mo, Zn (F AAS)	GF AAS	69
Serum	protein pptn. with CCl ₃ COOH	Cu, Fe, Zn	ICP MS	70
Serum	diln. with 1% HNO ₃	B, Mo, Sn, Zn	ICP MS	71
Serum (0.5–1 ml)	HNO ₃ –HClO ₄ (bomb)	Cd, Co, Cu, Fe, Mo, V, Zn	ICP AES ²	72
Serum (1 ml)	HNO ₃ –HClO ₄ (bomb)	Ba, Cu, Fe, Sr, Zn	ICP AES	73
Serum	HNO ₃ –HClO ₄ –H ₂ O ₂	Cd, Hg, Sb	RNAA ³	74
Urine	diln. with 2% HNO ₃	Cd, Hg, Sb	ICP MS	75
Urine		Cd, Cu, Pb, Zn	ETV-ICP AES ²	23
Urine CRM	acidified: 1% HNO ₃	As, Cd, Cr, Cu, Pb, Ni, Mn, Se, Zn	ICP AES	76
Urine CRM	HNO ₃ (microwave, bomb)	Cd, Cu, Pb	FI ID ICP MS	77
Milk, urine CRM (10 ml)	H ₂ SO ₄ –HNO ₃ , H ₂ O ₂ (microwave assisted)	As, Ba, Cd, Cu, Fe, Mg, Mn, Sr, Zn	ICP AES	78
Human milk		As, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Sb, Se, Zn	INAA RNAA ²	79
Saliva (5 ml)	HNO ₃	Al, Cr, Cu, Fe, Mn, Si, Sr, Zn	GF AAS	80

Separation/preconcentration by: ¹ extrn. of Fe as FeCl₄⁻ (MIBK), sorption of DBDTC complexes; ² sorption on poly(dithiocarbamate) resin; ³ extrn. with 4-(5-nonyl)pyridine (benzene).

Sampling and storage

Trace element contamination of sampling and storage equipment (collection tubes, stainless steel needles, Teflon catheters) used in blood and serum analyses was evaluated [69,81,82]. Significant contamination (Fe, Mn, Co, Cr, Ni) is observed in blood samples collected with disposable steel needles; the use of a polypropylene catheter [81] or siliconized needles is recommended instead [69]. A phlebotomy tube designed specifically for ultratrace metal analysis in serum has been evaluated [83]. Urine is easily sampled on a regular basis and can be analyzed by various techniques where liquid samples are readily accommodated. Storage and pre- and post-NAA treatment of urine samples for the determination of a number of elements have been summarized [84]. Representative saliva samples are difficult to be sampled since the composition depends on many biological factors. Saliva sampling has been discussed in detail [80]. The possibility of vertical gravitational fractionation of the organic fractions of saliva to which the metals are bonded during centrifugation has been emphasized [80]. Human milk is withdrawn by means of glass ball-type syringes previously decontaminated through rinsing with dilute HNO_3 . Aliquots obtained during the same day are pooled in order to counterbalance the diurnal changes in element concentrations. Storage at $+5^\circ\text{C}$ for 5 days is allowed but -30°C is required for longer periods [85]. Prior to analysis the milk is lyophilized for better homogenization and to facilitate the subsequent destruction of the organic matter. Seminal fluid was collected in a metal-free glass container. Following the semen liquefaction (15 min), spermatozoa were separated from seminal fluid by centrifugation and transferred into an polypropylene microtube and stored at -20°C until analysis [86].

Sample handling prior to analysis

Blood and serum contain large amounts of proteins (60–80 mg/ml) and dissolved salts (*ca* 10 mg/ml). In GF AAS direct introduction of blood samples is inadvisable due to (i) difficulty of pipetting microlitre volumes of viscous blood (wetting of the tips and settling of red cells), (ii) soaking of the sample into the carbon rod or tube, (iii) foaming, frothing and fogging of the quartz windows and (iv) build-up of carbonaceous residue within the furnace [88]. In ICP techniques clogging of the pneumatic nebulizer, of the central tube of the torch and of the entrance aperture of the sampling cone (in ICP MS) can take place. These phenomena make a treatment of the sample necessary before its introduction into most of analytical instruments. Dilution, deproteinization and acid digestion

are the most common. Dilution (5–10-fold) with 1–2% HNO_3 reported for serum [65, 66, 71] and urine [75, 76] is particularly suitable for ICP MS where the dilution factor can be tolerated. Dilution of blood gives rise to a slow precipitation of red cell membranes and produces a turbid heterogeneous suspension after about 15 min [87]. The use of the surfactant Triton X-100, unlike water, causes complete lysis of the blood cells, minimizes frothing, reduces the sample–graphite interfacial tension, improves the contact between the sample and furnace wall or platform, exerts no chemical effects on samples and standards and provides a clear solution [88]. To prevent precipitation of proteins buffering in the pH range 8–9 is necessary; an EDTA–ammonia mixture was used giving the required pH value and keeping cations in the solution [89]. Deproteinization with HNO_3 [90] or CCl_3COOH [70] and analysis of the supernatant liquid were recommended. Various deprotonizing agents have been compared [90]. Digestion with easily purified HNO_3 is recommended [63, 80]. HClO_4 may be added to complete the attack [62, 72, 73]. Closed vessels are recommended to reduce contamination. A microwave heated, flow-through digestion device for *on-line* preparation of milk, whole blood and urine has been developed [91].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS analysis for body fluids was reviewed [92]. Direct analysis of micro-volumes (5–50 μl) of undiluted body fluids (serum, urine, saliva, cerebrospinal fluid) using standard additions and peak area calibration is unmatched for most elements [93–97]. Details about matrix modification and possible interferences for particular elements can be found in Part III. Problems encountered in the direct determination of Cd, Co, Cr, Ni, Tl and Pb in urine by GF AAS have been discussed [98]. Direct determination of minor (Fe, Cu, Zn) elements in cerebrospinal fluid by FAAS with FI sample introduction has been developed [99]. Calibration and reference samples in trace analysis of serum by GF AAS have been discussed [100].

Atomic emission spectrometry

Several elements (e.g. Zn, Sr, Ba, Al, Li) can be easily determined by ICP AES or DCP AES whereas Cu and Fe are near detection limits of most of the instruments for the analysis of serum [52, 62, 73, 101] and amniotic fluid [102]. ICP AES is a rapid screening method for selected toxic elements in urine [76]. A series of elements has been determined in urine [76, 101] on acidification but generally for transition metals decomposition and sorption on a resin are required [72].

Other techniques

ICP MS is an excellent method for semiquantitative analysis of body fluids (saliva, blood, serum) [103]. A 5–10-fold dilution was found to be a good compromise between detection limit required and salt concentration problems [65,66,71,104] for serum and urine [75]. ICP MS [105, 106] and high resolution ICP MS [107] in clinical analysis have been evaluated. Neutron activation analysis played a decisive role for the establishing the normal levels in blood and serum. Radiochemical procedures were developed for whole blood [108,109], serum [74] and milk [79]. Total reflection XRF is suitable for multielement analysis of blood but digestion [63,110] and the removal of iron and alkali metals are often necessary [63]. Serum and other fluids can be analyzed on a small dilution [111].

10.2.2 Tissues

Soft tissues include human organs such as liver, heart or brain. Analytical methods usually involve a digestion step. Hard tissues include bones, hair, nail and urinary calculi. Hair and nail samples are useful indicators of the trace element burden of the body especially of toxic elements such as Hg, Cd, Pb, Se, Sb and As, and are used for forensic purposes. Urinary calculi consist of calcium oxalates and phosphates and uric acid and are analyzed for Al, Cu, Fe, Li, Mn, Mo, Pb, Sr, Zn [112]. Analytical procedures are summarized in Table 10.2.

Sampling

Sampling and sample pretreatment for analysis of human livers have been discussed [120]. The use of non-contaminating talc-free vinyl gloves, precleaned dust-free Teflon sheets and bags was recommended to prevent contamination. Titanium [120] or titanium nitride [121] knives should be used to avoid contamination by various constituents associated with a regular stainless steel scalpel (e.g. Ni, Co, Cr, Mo). This is also the case for the terminal part of the drill used in sampling of bone (contamination with Al) [122]. The main problem in hair analysis is external contamination which must be removed before analysis. A general disadvantage is the heterogeneity and the difficulty in obtaining truly representative samples. The distribution of trace elements in the lipid and non-lipid matter of hair has been discussed [123]. Owing to strongly reduced possibility of leaching or absorption, dry solid samples do not undergo significant changes in analyte concentration

TABLE 10.2

Multielement trace analysis of clinical soft and hard tissues

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Brain (0.1 g)	HNO ₃ (bomb)	Al, B, Co, Cr, Cu, Mn, Ni, Pb, Zn	ICP AES	113
Brain	<i>aqua regia</i>	As, Ca, Co, Cr, Cu, Fe, Hg, K, Na, Se, Zn	RNAA	114
Heart	H ₂ SO ₄ , HNO ₃ –HClO ₄ –H ₂ SO ₄	Se (HG AAS), Cu, Fe (GF AAS), Zn, Mg, K (FAAS)	GF AAS FAAS	115
Lung (5 g)	HNO ₃ (bomb)	Cr, Zn	RNAA ¹	21
Lung (5 g)	dry ashing, dissoln. in HNO ₃	Al, Cd, Cr, Cu, Mn, V, Zn	ICP AES	21
Liver (0.5 g)	HNO ₃ –HClO ₄	Co, Se, Mo (GF AAS), Cu (F AAS)	GF AAS ³	27
Soft (1 g)	HNO ₃	Fe, Cu, Zn, Cd, Sr, Y	ICP AES	116
Soft (0.5 g)	HNO ₃ (bomb, microwave assisted)	Al, Mn, Fe, Co, Cu, Zn, Rb, Sr, Mo, Cd	ICP MS	117
Hair	HNO ₃ –HClO ₄ –H ₂ O ₂	Hg, Cd, Sb	RNAA ²	74
Hair	vapour phase dissoln. with HNO ₃	Cu, Fe, Ba, Cs, Li, Mn, Rb, Sr	F AES	20
Hair (0.02 g)	HNO ₃	Al, Cd, Cu, Pb (GF AAS), Zn (F AAS)	GF AAS FAAS	118
Hair (0.1 g)	HNO ₃ –HClO ₄	Cu, Fe, Ni, Pb, Zn	ED XRF ⁴	26
Urinary calculi (0.25 g)	HNO ₃ –HClO ₄ (microwave)	Al, Cu, Fe, K, Li, Mn, Mo, Na, Pb, Sr, Zn	ICP AES	112
Urinary calculi (20–50 mg)	HNO ₃ (bomb)	Cd, Cr, Ni, Pb	GF AAS	119

Separation–preconcentration by: ¹ sorption on Chelex-100; ² extrn. with 4-(5-nonyl)pyridine (benzene); ³ extrn. with APDC (CHCl₃); ⁴ copptn. with APDC.

during storage. Hence, the most practical method for storage is lyophilization in which, after a fast-freezing process, the water content is slowly eliminated. The contamination hazard from container walls and changes in the mean composition are smaller than for fluids.

Decomposition

All soft human tissues were soluble in HNO_3 except liver and spleen samples where 0.5 M HCl had to be used to dissolve the residue [116]. Microwave-assisted digestion is becoming standard for soft tissues [117, 124] and is indispensable for the decomposition of bones and urinary calculi [112]. The effect of sample preparation on the determination of Cu, Mg, Pb and Cd in bone has been discussed [122]. *Aqua regia* is recommended for dissolving ashes with a high content of phosphates (e.g., ashed bone tissue). Dry and wet ashing have been compared for hair analysis; dry ashing can be used for Zn, Cu and Mn determination but wet dissolution in HNO_3 must be used for Fe determination [125]. Urinary calculi were decomposed in HNO_3 under pressure [119].

Determination

On decomposition the solution does not differ in composition from that of body fluids and can be analyzed by any instrumental technique. ICP AES and INAA or RNAA were compared for the determination of trace elements in human lung tissue [21,126]. Small biases were observed for Fe and Zn in the comparison of ICP MS and standard AAS methods for the determination of trace elements in soft human tissues; generally good agreement was achieved [117]. Hair presents a simpler matrix than blood or tissue for NAA. It is possible to determine short-lived nuclides of Na, Ca, Mg, Al and Mn in hair [127] and skin [128]. Determination of trace elements in human liver by NAA has been discussed [129].

10.3 ECOLOGICAL MATERIALS

10.3.1 Plant materials

Vegetation is used in biogeochemical prospecting for mineral deposits and is a valuable indicator of environmental (soil and atmospheric) pollution. Tree rings are considered to be archives of environmental pollution [130,131]. Leaves are analyzed for airborne deposition. The edible leaves and those used as tobacco have an impact on human health. Analytical methods are summarized in Table 10.3.

TABLE 10.3

Multielement analysis of plant materials

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Tree rings, bark, foliage	dry ashing, dissolution in HNO_3	Cd, Cu, Pb	GF AAS, FAAS	130
Tree rings, bark	50% H_2O_2 (bomb)	Al, As, Ba, Cu, Fe, Ge, Mn, Si, Sr, V, Zn	ICP AES	131
Tree rings, needles, phloem, roots	HNO_3	Ba, Cd, Cu, Fe, Mn, Pb, Sr, Zn	ICP AES, TXRF	132
Tree leaves (1 g)	$\text{HNO}_3\text{--HClO}_4$	Al, Co, Cu, Fe, Mn, Ni, Sb, V, Zn	FAAS	133
Grass (0.4 g)	$\text{HNO}_3\text{--HF}$ (bomb)	As, Ba, Cr, Cu, Ga, Ni, Pb, Rb, Se, Sn, Zn Cd, Co, Cr, Cu, Ga, Mo, Ni, Pb, Rb, Se, Sr, V, Zn, Zr	ED XRF ICP AES	134
Tea leaves	$\text{HNO}_3\text{--H}_2\text{SO}_4$	Al, Ca, Cu, Mg, Mn, Ni, Zn	ICP AES ⁵	135
Tea leaves	$\text{HNO}_3\text{--H}_2\text{SO}_4$	Ca, K, Mg, Mn, Zn	FAAS ⁵	135
Tea leaves	$\text{HNO}_3\text{--H}_2\text{SO}_4$	Cd, Cu, Ni, Pb	GF AAS ⁵	135
CMRs (animal feeds) (2 g)	Kjeldahl dissolution	Fe, Mn, Zn	ICP AES	136
CRMs (0.1–1 g)	LTA, $\text{HNO}_3\text{--HF}$	Ba, Cd, Cu, Fe, Ga, Ni, Pb, Rb, Sr, Tl, Zn	ID MS ¹	137
CRMs (0.5 g)	$\text{HNO}_3\text{--HCl}$ (microwave)	Cd, Cu, Pb (GF AAS); Fe, Mn, Zn (FAAS)	FAAS GF AAS	138
CRMs (0.25 g)	$\text{HNO}_3\text{--HF--H}_2\text{O}_2$ (microwave)	Al, As, Be, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Rb, Sr, Zn	DCP AES	139
CRMs (0.4 g)	$\text{HNO}_3\text{--HClO}_4$ (bomb)	Cd, Co, Cu, Mo, Ni; Pb	ICP AES ⁶	24
CRMs	dissolution with TMAH–EDTA	Cu, Fe, Mn, Na, Ni, Sr, Zn	ICP AES	140

continued

TABLE 10.3 (*continuation*)

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
CRMs (0.3 g)	H ₂ SO ₄ -HBr-H ₂ O ₂	Cd, Co, Cr, Mo	RNAA ³	141
CRMs (0.1 g)	microwave assisted	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	ETV ICP MS	142
CRMs	HNO ₃ -HCl-HClO ₄ -HF (microwave assisted)	Ca, Cu, Fe, K, Mn, Mg, Na, Zn	FAAS, FAES	143
CRMs (0.15 g)	HNO ₃ -HCl-HClO ₄ -HF (microwave assisted, bomb)	Al, Cu, Fe, Mn, Zn	ICP AES	144
CRMs (0.1 g)	HNO ₃ -HCl-HClO ₄ -HF bomb, microwave	Cd, Co, Cu, Ni, Pb	ICP MS	145
CRMs (0.5 g)	HNO ₃ -H ₂ O ₂	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se	STPF AAS	146
Plant	HNO ₃ -H ₂ O ₂ (microwave assisted)	Ba, Mn, Zn	ICP AES	147
Plant (0.15 g)	lyophilization	Ag, As, Cd, Cr, Mo, Se, Sb, Sn	RNAA ²	148
Biotissue (0.1 g)	vapour-phase acid decomposition, bomb	Ca, Cd, Cu, Fe, Mg, Sn, Zn	ICP AES	149
Biotissue (0.4 g)	HNO ₃ -HClO ₄ (bomb)	Cd, Co, Cu, Mo, Ni, Pb	ICP AES ⁶	150
Biosamples	HNO ₃ (bomb)	As, Ba, Co, Cr, Cs, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Sr, Zn	ICP MS	151
Biotissues (0.1-0.4 g wet)	HNO ₃ , bomb	Ag, Cd, Co, Cu, Fe, Na, Mg, Mn, Mo, Rb, Se, Sr, Zn	ICP MS	152
Biotissue	H ₂ SO ₄ -HNO ₃ -H ₂ O ₂	As, Cd, Cu, Hg, Mo, Sb, Se	RNAA ⁴	153

Separation-preconcentration by: ¹ electrolysis; ² multistep procedure; ³ anion exchange,, then on Chelex100; ⁴ extraction with Zn(DDTC)₂ in CHCl₃; ⁵ extraction with APDC-DDTC (CHCl₃), then back-extraction into a Hg(II) solution; ⁶ coprecipitation with APDC.

Sampling

Not only does the metal content vary with the species but the metal is unevenly distributed within the plant or tree. The same sections or parts (leaves, needles etc.) must be collected for analysis. Seasonal variations in concentrations must also be taken into account. All samples of tree leaves were washed with 5% EDTA solution and then with deionized water; this washing procedure is necessary to remove the particulate matter adhering to the surface so that the heavy metals absorbed by the tissue from the atmosphere can be distinguished from those weakly bound onto the surface [133].

Direct analysis

Direct analysis is important for rapid screening. It can be done by pressed pellet ETV ICP AES [154] graphite cup insertion [155] or a slurry technique [156–162]. The use of milling aid (alumina) was recommended for preparation of slurries to obtain small particles suitable for analysis [156]. Slurries of plant samples (dried or partly carbonized) were analyzed by FAAS and ICP AES for Al, Ba, Cd, Cu, Mg, Zn and Cd with precision and accuracy of 7–10% down to the 1 ppm level [157–159,161]. Slurry ETA AAS of pine needles has been described [162]. Slurry sampling of biomaterials has been reviewed [160]. Sorption of metals by algae and their slurry sampling has been discussed [163].

Digestion

Cellulose-containing samples (e.g. wood) can be dissolved under pressure in 50% H_2O_2 [131]. A microprocessor-controlled high pressure decomposition of agricultural samples has been described [164]. Microwave-assisted HNO_3 – H_2O_2 digestion was recommended for the preparation of botanical samples [147]. A rapid microwave dissolution method (HCl – HNO_3 in closed PTFE beakers) for the determination of trace elements in plant material has been proposed [138]. Digestion of grass by H_2O_2 under alkaline conditions, subsequent to initial enzymatic hydrolysis, has been recommended [165]. Tetramethylammonium hydroxide was not able to give a clear solution from botanical samples, but the supernatant after digestion in the presence of EDTA was used for determination 12 major and trace elements [140]. The microwave dissolution technique was examined in order to establish a sample decomposition method without the use of HClO_4 and/or H_2SO_4 , which are known to produce various molecular species that overlap with several important isotopes in ICP MS analyses. It was possible to decompose most of the plant material nearly completely by HNO_3 alone [166].

Determination

Graphite furnace AAS and ICP AES are equally popular for the analysis of plant materials. The suitability of FAAS and ICP AES for the determination of Pb, Cu, Cd, Cr, Zn and Ni in plant has been compared [167]. Application of ICP MS has been discussed [153]. Non-linear spectral interferences for simultaneous ICP AES of plant samples [168] and effect of pH and digestion conditions on Chelex-100 separation of trace elements from tissue digests prior to ICP AES have been discussed [169]. Spectral interferences encountered in the analysis of biomaterials by ICP MS were studied in detail and correction procedures have been proposed [170]. Instrumental NAA and RNAA were used for the multielement analysis of botanical [171–174] reference materials. Direct analysis of the growth rings of trees (K, Ca, Ti, Mn, Fe, Ni, Cu, Zn) was done by XRF [175].

10.3.2 Animal tissues

Analytical methods recently developed for the analysis of animal tissues are summarized in Table 10.4.

TABLE 10.4

Multielement trace analysis of animal tissues

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
CRM fish (0.5–1 g)	HNO ₃ –H ₂ O ₂ (microwave assisted)	As, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn	ID ICP MS ICP MS	176
Fish (0.25 g)	HNO ₃ –HClO ₄ (microwave assisted)*	Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn, Zn	ICP MS	177
Shellfish (12.5 g)	HNO ₃ (microwave assisted)	Cd, Cr, Cu, Pb, Zn	FAAS	178
Shellfish	HNO ₃	Cd, Cu, Cr, Ni, Pb, Zn	ICP AES FAAS	167
CRM (lobster), fish, scallop (0.5 g)	HNO ₃ , HNO ₃ –H ₂ O ₂	As, Cd, Cu, Pb, Se	GF AAS	179

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
CRM (lobster) (1.5 g)	HNO ₃ -H ₂ O ₂ (microwave)	Cr, Cu, Zn, Cd, Ni, Mo, Sr, Hg, Co	ID ICP MS	180
CRM (lobster) (0.25 g)	HNO ₃ -H ₂ O ₂ (microwave)	As, Cd, Co, Cr, Mn, Mo, Ni, Pb, Se, V, Zn (GF AAS); Cu, Fe, Sr (FAAS)	GF AAS FAAS	18
CRM (lobster) (0.1 g)	HNO ₃	V, Cr, Mn, Ni, Cu, Zn, As, Sr, Cd, Pb	ICP MS	35
CRM (lobster) (0.25 g)	vapour phase dissoln. with HNO ₃	Cu, Fe, Sr, Zn (FAAS), As, Cd, Co, Cr, Mn, Mo, Ni, Pb, Se, V (GF AAS)	GF AAS FAAS	181
Mussel (0.3 g)	HNO ₃	Cd, Cu, Fe, Pb, Zn	FAAS	182
CRMs (oyster, animal tissue) (0.2 g)	HNO ₃ -H ₂ O ₂ or HNO ₃ (microwave)	22 elements	ICP MS	34
CRM (oyster) (0.1-1 g)	HNO ₃ -HF (bomb) or LTA, dissoln. in HNO ₃ -HF	Fe, Ni, Cu, Zn, Ga, Rb, Sr, Cd, Ba, Tl, Pb, Cr	ID MS ²	183
Shrimp (1-5)	HNO ₃ (microwave)	Fe, Cu, Cd	GF AAS	19
Oyster (0.5-0.6 g)	HNO ₃ -HF (bomb) or LTA	Fe, Ni, Cu, Zn, Ga, Pb, Sr, Cd, Ba, Tl, Pb	ID TI MS	184
Shrimp (0.25-0.5 g)	HNO ₃ (microwave)	Fe, Cu, Cd	GF AAS	185
Scallops (0.75 g)	HNO ₃	Cd, Cr, Co, Cu, Au, Fe, Pb, Mn, Hg, Ni, Ag, Zn	FAAS ³	186
Marine tissues (0.1 g)	HNO ₃ (microwave assisted, bomb)	Cu, Zn, Cd	GF AAS, FAAS	187
Marine tissues, CRMs (1 g)	HNO ₃ (microwave assisted, bomb)	As, Cd, Pb	ICP AES ICP MS	188
Marine tissues (0.25 g)	HNO ₃ (microwave assisted, bomb)	As, Cd, Co, Cr, Mn, Mo, Ni, Pb, Se, V	GF AAS	189
CRM (animal tissue) (1 g)	H ₂ SO ₄ -HNO ₃ , H ₂ O ₂ (microwave assisted)	As, Ba, Cd, Cu, Fe, Mg, Mn, Sr, Zn	ICP AES	78

continued

TABLE 10.4 (continuation)

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Animal (0.2–0.5 g)	HNO ₃ –H ₂ SO ₄ –HClO ₄	Cd, Cu, Fe, Mn, Pb	GF AAS	190
Animal (0.1–1 g)	HNO ₃ –H ₂ SO ₄ –HClO ₄	Cu, Fe, Mn, Zn	ICP AES	191
Animal, CRM (liver) (0.2–0.3 g)	leaching with HNO ₃	Cu, Fe, Mn, Zn	ICP AES GF AAS	192
CRMs (animal tissue) (0.5 g)	HNO ₃ (bomb, microwave assisted)	Al, Cd, Fe, Co, Cu, Mn, Mo, Rb, Sr, Zn	ICP MS	117
Feces	HNO ₃ –H ₂ O ₂ or HNO ₃ –H ₂ SO ₄	Cu, Fe, Zn	ID ICP MS ICP MS ¹	32
Rat, CRM (liver) (0.1 g)	HNO ₃ , HClO ₄ bomb	As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Si, Sr, Zn	ICP AES	62
Rat (0.5 g)	HNO ₃ (microwave assisted)	27 elements	ICP MS	193
Rat liver	homogenization with HCl	Cu, Mn, Zn	FAAS	194
Bovine liver (0.5 g)	leaching with HNO ₃	Cd, Cu, Fe, Mn, Mo, Zn	ICP AES	195
Larvae (1 specimen)	HNO ₃ , HNO ₃ –H ₂ O ₂	Cd, Cu, Pb, Zn (F AAS)	GF AAS	42
Octocorals (1 g)	HNO ₃ (microwave assisted)	Cd, Cu, Ni, Pb (GF AAS), Zn (FAAS)	GF AAS FAAS	196
CRM (bovine liver) (0.5 g)	HNO ₃ (microwave assisted)	Ag, Al, As, Cd, Co, Cu, Fe, Hg, Mn, Mo, Pb, Rb, Sb, Se, Sr, Ti, V, Zn	ICP MS	27
Liver (0.4 g)	HNO ₃ –HCl–HClO ₄ (bomb)	Cd, Cu, Mn, Pb	ICP AES	197

*Special decomposition procedure for Hg detn.

Separation/preconcentration by: ¹ precipitation with APDC (Cu, Zn), as Fe(OH)₃ (Fe);

² electrolysis; ³ removal of Na⁺ on Sb₂O₅aq.

Solubilization and leaching

No losses of Fe, Zn, Cu, Mn, Co, Cd, Hg, Pb, As and Se were observed during lyophilization of rat liver [198]. Quaternary ammonium hydroxides (e.g. TMAH) are capable of dissolving animal tissue offering relatively low sample dilution, but suffer from high blank values resulting from the reagent [186]. Acid leaching is expected to prove effective for many tissues since biological systems share a common metal-binding mechanism. Leaching with HNO_3 -HCl was found to be successful for the determination of Al, Cd, Cr, Cu, Zn, Fe and Sn in food samples [199]. Partial digestion with HNO_3 (105°C, 20 min) was found to be sufficient for complete release of Cu, Fe, Mn and Zn from animal tissue [192]. A simple digestion with HNO_3 followed by filtration of the undigested lipids was found to be suitable for the decomposition of bovine liver for the ICP AES determination of Cd, Cu, Fe, Mn, Mo and Zn [195]. Homogenization of rat liver with HCl was used for extraction of Cu, Mn and Zn; after centrifugation the supernatant fluid served for FAAS determination [194].

Complete digestion

Four digestion procedures, dry ashing, hot-block, high pressure and microwave heating digestion, have been compared for marine tissue samples [185]. Microwave digestion in GF autosampler cups was recommended for rapid dissolution of sub-milligram amounts of marine tissue [185]. Microwave digestion of shellfish was compared with wet and dry digestion and was shown to give comparable results being at the same time faster, safer and easier to use [178]. Acid digestion in various types of microwave-assisted devices has been discussed [200, 201]. Microwave PTFE bomb dissolution with H_2SO_4 - HNO_3 [202] and HNO_3 - H_2O_2 has been proposed for animal tissue [176,180]. An automated wet digestion procedure of animal tissue with a mixture of HNO_3 - HClO_4 - H_2SO_4 (5+1+1) under reflux enabled to obtain complete digestion to be obtained in a single stage [190,203]. The Parr bomb was preferable for the simultaneous determination of metals in soft animal tissues [62]. Vapour-phase acid decomposition of small biosamples (0.1 g) in a mini quartz sample holder inserted in a commercial high pressure vessel has been proposed [149].

Determination

Some elements (e.g. Zn, Fe, Cd, Cu, Pb) can be determined at environmentally relevant levels directly by FAAS in the sample digest

[17,18,181,182,186,194]; for a series of others GF AAS is the dominant technique [17,19,179,181,185,190,192] whereas ICP AES is equally efficient [62,191,192,195,197]. ICP MS is gaining popularity owing to its versatility [34,35,117,177,193] and isotope dilution capability [32, 176,180]. INAA of marine tissues has been reported [204,205]. A sequential procedure for determination of 44 elements in marine bivalves using INAA, prompt gamma activation and XRF has been developed [205].

10.4 FOODSTUFFS

Interest in foodstuffs analysis for trace elements is related to the need to ascertain that analyte levels comply with specified limits as a consequence of previous considerations of the toxicological and the nutritional properties of the elements. Mixed diet composites are used to estimate the intakes of nutrient and toxic elements, especially for a number of elements (such as Cd, Cr, Hg and Mo) that occur at low concentrations in individual food products. Analysis of foodstuffs has been reviewed [206] with particular emphasis on AAS [207], HG AAS in wine and beverages [208], ICP AES [31], ICP MS [209,210] and NAA [211–214]. Analytical methods recently developed are summarized in Table 10.5.

TABLE 10.5
Multielement trace analysis of foodstuffs

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Mixed diet (~0.6 g)	HNO ₃ –H ₂ SO ₄ – HClO ₄	Al, Cd, Co, Cu, Fe, Mo, Mn, Ni, Sr, Zn	ICP AES ¹	215
Mixed diet (2 g)	dry ashing, dissoln. in HNO ₃	Cu, Fe, Mn, Zn	FAAS	215
Wine, must (10–50 ml)	H ₂ O ₂	Al, Cd, Co, Cr, Cu, Fe, Mn, Pb, V, Zn	ICP AES	216
Yeast (0.5–1.5 g)	H ₂ O ₂ –H ₂ SO ₄	Al, Cd, Co, Cr, Cu, Fe, Mn, Pb, V, Zn	ICP AES	216

Sample (amount)	Decomposition	Elements determined	Detection technique	Ref.
Vegetables (1 g)	dry ashing, HNO ₃ (microwave assisted)	Fe, Mn, Zn	FAAS	217
Crops, CRMs (spinach, wheat)	dry ashing with 40% H ₂ SO ₄	Al, Cd, Cr, Mo, Ni, Pb, Rb, Zn	ICP MS	218
SRMs (citrus leaves, corn, milk, bovine liver) (1 g)	HNO ₃ -HCl (bomb)	B, Ca, Fe, Mg, Mn, Pb, Sr, Zn	ICP AES	164
CRMs (food) (0.5 g)	HNO ₃ bomb	As, Cd, Ce, Co, La, Mo, Ni, Pb, Sn, Tl	ICP-MS	219
CRM (foodstuffs), feces (0.5-1 g)	HNO ₃ -HCl (microwave assisted, bomb)	Cu, Fe, Mn, Zn	ICP AES	220
Food (0.1-1.0 g)	HNO ₃ , H ₂ O ₂ (microwave assisted)	Cu, Fe, Mn, Zn	FAAS	221
Food (2-10 g)	leaching with HNO ₃ -HCl	Al, Cr, Cu, Fe, Sn, Zn	FAAS	199
Food (5 g)	fusion with LiBO ₂	Al, Ba, Si, Sr, Ti	ICP AES	222
Infant formula (2 ml)	HNO ₃ -H ₂ O ₂ (bomb)	Cu, Sn, Zn (F AAS) Cr, Ni, Pb (GF AAS)	FAAS GF AAS	223
Commercial milk		As, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Se, Sb, Zn	INAA RNAA ²	79
Milk	HNO ₃ -HClO ₄	Cd, Co, Ni, Pb	GF AAS ²	223
Milk (1 ml)	HNO ₃ , HClO ₄ , H ₂ O ₂	Cr, Fe, Mn, Zn	ICP MS	224
Milk	dry ashing, HNO ₃	Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Zn (ICP AES); Li, Pb (GF AAS)	ICP AES GF AAS	85

¹ Matrix removal on Chelex 100; ² precipitation with APDC with Cu and Fe carriers.

Direct analysis

The procedure combining slurry sample introduction with an oxygen ashing step that helps to remove much of the organic matrix before the atomization step was used for the determination of Cd, Cu and Pb in a variety of foodstuffs [225]. Comparison of the direct solid and slurry sampling GF AAS analysis of milk powder showed that the direct solid sampling is suitable for refractory (Cr, Mo) and slurry for volatile (Cd, Se, Pb, Zn) elements [226].

Decomposition

Food samples with masses up to 5 g have been prepared by HNO_3 – HClO_4 mixtures in a microwave system. Analysis of foodstuffs (As, Cd, Cr, Cu, Sb, Se, Zn) after HNO_3 – HClO_4 decomposition by RNAA has been reported [227]. A comparison between INAA, RNAA and ICP MS for food samples has been presented [228]. Digestion methods for AAS of foods have been compared [229]. Dissolution of cocoa under stopped-flow, high pressure conditions has been evaluated [230].

Determination

Several elements (e.g., Cu, Fe, Mn, Zn) can be determined by FAAS [199,217,221,223,231]. Problems with direct GF AAS analysis of edible oils for Cu, Cd, Sn, Pb, Cr, Mn, Fe, Co and Ni (smoke, high background, poor reproducibility) were circumvented by grooving the tube and coating it with tantalum or niobium and/or matrix modification with alcoholic KOH [232]. Traces of Fe, Zn, Cu, Mn and Sr can be readily determined by ICP AES in most foodstuffs [55,183] whereas others such as Al, Mo, Ni, Cr, Pb, Se, As, Cd, Co, V and Hg require a separation–preconcentration step [183]. The use and limitations of ICP AES in wine analysis have been discussed [216]. The potential of ICP MS in food analysis has been evaluated and the effects of major components (Na, Mg, P, K, P, Ca) on the determination of traces (Al, Cr, Zn, Mo, Cd, Pb) have been studied [218]. The use of ICP MS in human nutrition and toxicology has been discussed [233]. Application of ICP MS to accurate isotopic analysis for human metabolic studies has been evaluated [32]. Details can be found in chapters for Fe, Cu and Zn. Absorption and bioavailability of mineral nutrients have been studied by TI MS, ICP MS and FAB MS [234]. INAA is fairly insensitive because of Na, Br, K and P activities which should be removed by RNAA to obtain an up to a 2000-fold gain in sensitivity. Foodstuffs such as sugar, fat and beverages have to be irradiated in a lower neutron flux because the heating

in the higher flux results in leakages due to the food outgassing. Direct energy-dispersive XRF was able to reach detection limits down to 1 ppm for As, Rb and Zn in milk powder [235].

10.5 SPECIATION

Selective determination of organoelement compounds in biological matrices is a rapidly emerging field in speciation analysis. The species of concern include compounds of metals with high affinity for sulphur (e.g. Zn, Cu, Cd, Hg, Pb, Bi, Au) which are able to associate with the cysteine thiol groups, anthropogenic organometallic contaminants (e.g., organolead and organotin) and products of natural transformation of Hg, As and Se. The problems are discussed in Part III. Chemical speciation in biology and medicine has been discussed [236–238]. Enzymolysis procedures for speciation studies have been discussed [239,240].

Metallothioneins (MTs) are low weight proteins devoid of aromatic amino acids which are remarkably stable with regard to proteolytic digestion and thermal denaturation and show no detectable enzymatic activity [241]. The interest in speciation of protein-bound metals is also associated with the ability of some organisms (when exposed to heavy metals) to synthesize high levels of metallothioneins which are responsible for trace metal detoxification. Metallothioneins show extremely high (*ca* 10%) sulphur and metal (primarily Zn, Cd, Cu(I)) content. Despite the chemical similarity, the particular metals are associated with different sites of metal-binding ligands. Metallothioneins are divided in three groups [241]: (1) polypeptides related in primary structure to equine renal MT, (2) polypeptides with no correspondence to mammalian forms and (3) polypeptides from plants composed of atypical γ -glutamylcysteinyl moieties. Mammalian MTs can be divided into two subgroups MT-1 (carries two negative charges) and MT-2 (three negative charges) at neutral pH. They can further represent mixtures of different isoforms.

Size-exclusion chromatography is the dominant technique for the study of metal binding to proteins and metal detoxification in marine organisms [242–244]. Furthermore, the separation of some thioneins by reversed-phase [245–249] and anion-exchange [250,251] chromatography has been reported. Capillary zone electrophoresis was widely used [249,252–254] but adsorption problems of non-analyte proteins on the capillary wall prevented the analysis of real samples [253,254] requiring

a preseparation step [254]. Gel electrophoretic techniques are more suitable [255-257]. Speciation of toxicologically important transition metals using ion-chromatography with ICP MS has been discussed [146]. Analytical methods are discussed in more detail in Part III.

10.6 QUALITY ASSURANCE

The close relevance of biomaterials analysis to human health prompts the use of multilaboratory exercises for the purpose of quality assurance. Methods for toxic elements in food products according to Russian standards have been presented [258]. The development of laboratory control samples for the determination of nutrient elements has been discussed [191,259]. Experiences from the round-robin exercises in Germany have been reported [260]. Selected multilaboratory round-robin exercises are summarized in Table 10.6.

TABLE 10.6

Survey of round-robin exercises for trace analysis of biological materials

Sample	Elements determined	Detection techniques	No. of labs	Ref.
Human albumin	Al, Ba, Cr, Cu, Fe, Mn, Mo, Ni, Se, Sr, V, Zn	FAAS, GF AAS, ICP MS, ETA AES, ICP AES, VIS	6	261
Plant tissue	Al, B, Cu, Fe, Mn, Zn	ICP AES	14	262
Protein solutions	Al, Cr, Cu, Fe, Mg, Mn, Ni, Se, Zn	FAAS, GF AAS, ICP AES, ICP MS	7	61
Food samples (wheat flour, milk powder, potato, pork, mixed diet)	Cd, Cu, Fe, Mn, Mo, Se, Zn	FAAS, GF AAS	n.g.	263
Total diet	Cd, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Zn	CV AAS, GF AAS, ICP AES, AFS, INAA, RNAA, ID MS, ID ICP MS, VIS	21	264

Sample	Elements determined	Detection techniques	No. of labs	Ref.
Bovine serum	Al, Co, Cr, Cu, Fe, Mn, Mo, Ni, Se, V, Zn	FAAS, GF AAS, FAES, ICP AES, ICP AFS ID MS, NAA, VIS	12	229
Bovine teeth and meat powder	Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, Zn	CV AAS, ICP AES, DCP AES, NAA	n.g.	265
Mixed diet	Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Se, Zn	FAAS, GF AAS, ICP AES, ID MS, NAA, fluorometry	8	266
Oils, fats	Cu, Fe, Ni	GF AAS		267
Animal feeding stuff	Cu, Fe, Mn, Zn	FAAS	11	268
Narwhal liver and muscle	Cd, Cu, Cd, Hg, Pb, Se, Zn	FAAS, GF AAS, CV AAS, ICP AES, NAA	13	269
Human serum	Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Mo, Cd, Cs	FAAS, GF AAS, FAES, ICP AES, NAA, ID MS PIXE	22	270
Wheat flour	Cr, Cu, Fe, Mn, Mo, Ni, Se, Zn	FAAS, GF AAS, HG AAS ICP AES, DCP AES, NAA, VIS, fluorometry	15	271
Skim milk powder, pork meat, wheat flour	Cd, Hg, Pb	GF AAS, ID ICP MS	17	272

The primary role in the field of quality assurance is played by certified reference materials (*cf.* Section 8.4). The role of CRMs for human and animal tissues [273] and nutrition research [259,274–277] has been reviewed. Sources of error in the analysis of biomaterials have been exhaustively discussed and many CRMs listed [278]. Cryo-grinding equipment for the preparation of large quantities of RMs with low heavy metal contents has been developed [279]. An external quality assessment scheme for trace elements in body fluids has been presented [280]. The function of solid sampling GF AAS in the production of bovine liver has been discussed [281]. Preparation of the following

reference materials has been reported: tea leaves [282], bovine muscle powder [283], bovine teeth and meat powder [265], beech leaves and spruce needles [280], cabbage leaves [284], mussel tissue [285], cabbage and carnation [286], human hair powder [287], bovine muscle [288], bovine liver [288], bovine serum [289], pig kidney [288], mixed diet [266], total diet [290], plankton [291], tobacco leaves [292], dogfish flesh (DORM-1) and dogfish liver (DOLT-1) [293], codfish [107,294], human serum [270]. The work of the BCR [295,296], NIST [297–299], NIES [300,301], IAEA [302], IUPAC [303], Environmental Specimen Bank (FRG) [304,305] and Chinese institutions [306] in the field of preparation, certification and interlaboratory cooperative studies has been outlined. Lists of biological [307] and marine [308] reference materials have been given. The most important biological CRMs are listed in Table 10.7.

TABLE 10.7

Standard materials for determination of trace elements in biological matrices

Material	Description	Trace elements certified
NIES 1	pepperbush	As, Ba, Cd, Co, Cu, Pb, Ni, Na, Sr, Zn
NIES 3	chlorella	Co, Cu, Mn, Sr, Zn
NIES 7	tea leaves	Cd, Cu, Pb, Ni, Na, Zn
NIES 9	sargasso	As, Ag, Cd, Co, Cu, Fe, Mn, Pb, Rb, V, Zn
MAA1TM*	copepoda	Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Zn
DOLT1*	dogfish liver	As, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mg, Ni, Se, Zn, MeHg
DORM1*	dogfish muscle	As, Cd, Co, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Zn, MeHg
MAB3TM*	fish tissue	As, Ca, Cu, Fe, Hg, Mn, Pb, Rb, Se, Sr, Zn
TORT1*	lobster	As, Cd, Co, Cr, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Se, Sr, Sn, V, Zn, MeHg
LUTS1*	lobster	As, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Ag, Se, Sr, Zn, MeHg
	hepatopancreas (non defatted)	
NIST SRM 1515	apple leaves	As, Ba, B, Cu, Hg, Mn, Mo, Na, Ni, Pb, Se, Sr, V, Zn
NIST SRM 1547	peach leaves	B, Cu, Hg, Mn, Mo, Na, Ni, Pb, Se, Sr, V, Zn
NIST SRM 1548	total diet	Cd, Cu, Fe, Mn, Se, Zn
NIST SRM 1549	non-fat milk powder	Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn
NIST SRM 1566a	oyster tissue	Ag, As, Cd, Co, Cr, Cu, Mn, Hg, Ni, Pb, Se, Sr, U, V

NIST SRM 1567a	wheat flour	Al, Cd, Cu, Fe, Mn, Mo, Rb, Se, Zn
NIST SRM 1568a	rice flour	Al, As, Cd, Cu, Fe, Mn, Hg, Mo, Rb, Se, Zn
NIST SRM 1573	tomato leaves	As, Cr, Cu, Pb, Rb, Sr, Th, U, Zn
NIST SRM 1575	pine leaves	Cr, Cu, Pb, Hg, Rb, Sr, Th, U
NIST SRM 1577b	bovine liver	As, Cd, Co, Pb, Mn, Hg, Mo, Rb, Se, Ag, Sr, U, V
NIST SRM 8414	bovine muscle powder	Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Rb, Se, Sr, Zn
NIST SRM 8415	whole egg powder	Al, B, Co, Cr, Cu, Fe, Hg, Mn, Mo, Pb, Se, Sr, V, Zn
NIST SRM 8416	microcrystalline cellulose	Al, Co, Cu, Mo, Ni, Se
NIST SRM 8418	wheat gluten	Al, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sr, Zn
NIST SRM 8432	corn starch	Al, Cu, Mo, Ni, Se
NIST SRM 8433	corn bran	Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sr, V, Zn
NIST SRM 8435	whole milk powder	Ba, Cu, Fe, Mn, Mo, Pb, Rb, Se, Sr, Zn
NIST SRM 8436	durum wheat flour	Al, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sr, V, Zn
NIST SRM 8437	hard red spring wheat flour	Cr, Cu, Fe, Mn, Mo, Se, Zn
NIST SRM 8438	soft winter wheat flour	Cu, Fe, Mo, Se, Zn
BCR CRM 063R	skim milk powder	Cu, Fe, Pb, Zn
BCR CRM 150	skim milk powder	Cd, Cu, Fe, Hg, Pb
BCR CRM 151	skim milk powder	Cd, Cu, Fe, Hg, Pb
BCR CRM 184	bovine muscle	Cd, Cu, Fe, Hg, Mn, Pb, Se, Zn
BCR CRM 185	bovine liver	As, Cd, Cu, Hg, Mn, Pb, Se, Zn
BCR CRM 186	pig kidney	As, Cd, Cu, Hg, Mn, Pb, Se, Zn
BCR CRM 189	wholemeal flour	Cd, Cu, Fe, Mn, Pb, Se, Zn
BCR CRM 191	brown bread	Cd, Cu, Fe, Mn, Pb, Zn
BCR CRM 274	single cell protein	As, Cd, Co, Cu, Mn, Se, Zn
BCR CRM 279	sea lettuce	As, Cd, Cu, Pb, Se, Zn
BCR CRM 281	rye grass	As, B, Cd, Cu, Fe, Mn, Mo, Ni, Pb, Sb, SE, Zn
BCR CRM 402	white clover	As, Co, Mo, Se
BCR CRM 278	mussel tissue	As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn
BCR CRM 397	human hair	Cd, Hg, Pb, Se, Zn
BCR CRM 414	plankton	As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn
BCR CRM 422	cod muscle	As, Cd, Cu, Fe, Hg, Mn, Pb, Se, Zn
BCR CRM 060	aquatic plant	Cd, Cu, Hg, Pb
BCR CRM 061	aquatic plant	Cd, Hg, Pb
BCR CRM 062	olive leaves	Cd, Cu, Hg, Mn, Pb, Zn

*Issued by National Research Council (Canada).

The necessity for the development of reference materials for speciation analysis has been emphasized [309,310]; the activity of the BCR in this field has been presented [309]. Preparation of biological and environmental CRMs for this purpose has been discussed [310].

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Inorganic industrial materials

Trace elements (often at sub- $\mu\text{g/g}$ levels) affect the electrical, mechanical, optical and nuclear properties of high technology materials such as high-purity metals and alloys, semiconductors, advanced ceramics and their process intermediates. The high sample throughput and degree of automation required for industrial quality control favour direct multielement analytical techniques. In view of the lack of sensitivity of WD XRF below the 100 ppm level and the applicability of INAA to a few matrices only (Al, Si, Nb, Zr) the most popular are ablation MS techniques such as LA MS, GD MS, SS MS, exhaustively reviewed [1–3]. The difficulties with standardization, sample homogeneity and analysis at the ng/g levels (*cf.* Section 4.8.2) make wet chemical operations indispensable. This chapter deals with handling and multielement trace characterization of high technology industrial materials by means of analytical procedures that require at least one chemical step. Analysis for particular elements is discussed elsewhere in Part III. It must be emphasized that the information on the bulk composition needs often to be completed by surface, depth-profiling and microbeam techniques, especially in the field of modern electronics [3].

11.1 METALS AND ALLOYS

Metals are divided into ferrous (Fe, Cr, Mn, Ni, steels and ferroalloys), non-ferrous (Al, Cu, Pb, Sn, Zn), refractory (Mo, W, Nb, Ta, Ti, Zr, Re) and precious (Ag, Au and Pt-group metals) metals. They are analyzed as turnings, filings, shavings or fine wire. Prior to analysis they need to be brought into solution unless WD XRF, INAA or an ablation technique is used.

The dissolution of metals is an oxidation process. For metals with a

negative normal potential (E^0) the usual oxidizing agent is the H^+ ion supplied by an acid whereas for those with $E^0 > 0$ oxidizing acids are usually used. For metals undergoing passivation addition of HCl or HF is required. Anodic oxidation, especially in the presence of complexing electrolytes, speeds up the rate of dissolution, e.g., for noble metals, Nb, Ti and Zr [4] and has gained in popularity in the *on-line* FIA mode [5–9]. Microwave dissolution considerably reduces the dissolution time of metal and alloys but, since large amounts of gas are evolved during dissolution, gas venting and cooling the vessel prior to opening are recommended for the safety reasons [10]. Robotic preparation of metal samples for ICP AES is standard in industrial laboratories [11].

The major techniques used are ICP AES and ICP MS usually applied without any separation/preconcentration step. The latter may be necessary in the case of line-rich matrices and/or when sub-ppm detection limits are required. Graphite furnace AAS is likely to solve any particular analytical problem but is usually time consuming. Analytical techniques in metallurgical laboratories have been reviewed with special emphasis on AAS [12], ICP AES [13] and ICP MS [14].

11.1.1 Ferrous metals and alloys

This group includes Fe, Cr, Mn and Ni metals and their alloys, such as steels and ferroalloys (e.g. ferromanganese, ferrosilicon, ferrochromium). Selected analytical methods are summarized in Table 11.1.

TABLE 11.1

Multielement trace analysis of ferrous metals, alloys and related compounds

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Iron (5 g)	HF–H ₂ O ₂	anion-exchange	ICP AES	B, Mo, Nb, Sn, Ta, W, Zr	15
Iron	HCl–HNO ₃	copptn. as HMDTC complexes with Fe as collector	FAAS, ICP MS	Bi, Cd, Co, Cu, Hg, In, Mo, Ni, Pb, Sb, Sn, Te, Zn	16
Steel (0.1 g)	<i>aqua regia</i> , HClO ₄	matrix extrn. as FeCl ₄ [–] , extrn. of REE as nitrate complexes, cation exchange	RNAA	Ba, Ce, Hf, La, Nd, Pr, Sm, Zr	17

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref
Pb-Sb alloys (5 g)	HBr-Br ₂	matrix pptn. as bromide	FAAS	As, Bi, Cd, Co, Cr, Cu, Fe, In, Mn, Ni, Se, Tl, Zn.	54
Lead, Sn-alloys (0.4-1 g)	HBr-Br ₂	pptn. of Pb as PbSO ₄	FAAS	Ag, Bi, Cd, Fe, Ni, Cu, Zn	55
Lead, Pb-alloys (6 g)	HNO ₃	none	ICP AES	Ag, As, Bi, Cd, Cu, Fe, Cd, Mn, Ni	56
Tin (0.1 g)	HBr-Br ₂	none	GF AAS	Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Sr, V, Yb	57
Gallium (1 g)	HCl (gas)	volatn. as GaCl ₃ ; residue dissolved in HNO ₃	GF AAS	Al, Cd, Cu, Fe, Mg, Pb	58
Gallium (1 g)	HCl-HNO ₃	controlled dissolution	ICP AES, GF AAS	Ag, Bi, Cu, Fe, Ni, Pb	59
Gallium (1 g)	HCl	extrn. of GaCl ₄ (MIBK)	ICP AES GF AAS	Al, Ca, Cd, Co, Cu, Mg, Mn, Ni,,Pb, V, Zn	59
Gallium (n.g)	HCl-HNO ₃ (bomb)	extrn. with APDC	GF AAS	Cd, Co, Cu, Fe, Ni	60
Gallium (0.6 g)	n.g.	extrn. with DOTC		Bi, Ca, Cd, Cu, Fe, Mn, Mo, Ni, Pb, Si, Sn, Te, Zn	61
Gallium (1 g)	HCl-HNO ₃	extrn. of Ga with β,β'-dichloro- diethylether	GF AAS	23 elements	57
Indium (1 g)	HBr	extrn. of In with β,β'-dichloro- diethylether	GF AAS	21 elements	57

continued

Pure iron metal can be dissolved in HF-H₂O₂ [15,16] or by anodic oxidation [29]. Alkaline earths metals can be determined directly by FAAS. Prior to the determination of transition metals, the matrix should be separated, e.g. by electrodeposition on a Hg cathode [29], extraction as FeCl₄⁻ with DIPE [17] or anion exchange [15]. Alternatively, trace impurities can be extracted [30] or coprecipitated with dithiocarbamates [16]. Graphite furnace AAS, INAA and radiochemical proton activation analysis for trace analysis of cast iron for Sb, As, Bi and Pb have been compared [31].

Steels are ferrous alloys containing varying amounts of C, Ni, Cr, Mn, and other elements. Complete dissolution of steels is usually achieved with HCl-HClO₄-HNO₃, sometimes with the addition of (NH₄)₂S₂O₈ [32], HNO₃-HCl-HF [18] or *aqua regia* [19,20]. H₃PO₄ is used to digest steels rich in W (>0.5%) or when HCl would have volatilized specific trace constituents. Steels containing more than 1% of Sn require fusion. Analysis for As, B, Bi, Nb, Sb, Se or Te requires customized approaches discussed in Part III. Ferrotungsten is dissolved by a mixture of oxalic acid and H₂O₂ followed by a H₂SO₄-H₃PO₄ attack [33] whereas the latter mixture alone is sufficient to dissolve ferrochromium and ferromanganese [21]. Fusion with Na₂CO₃ or microwave-assisted digestion are rapid alternatives. Iron-based alloys spark when subjected to microwave radiation and the possible ignition of the H₂ gas evolved is a safety hazard. A thorough predigestion, filling under N₂-gas or open vessel digestion is required [18]. Microwave-assisted procedures have been developed [18,34]. Several elements (Al, Ca, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Sb, Si, Sn, Ti, V, W, Zn) can be determined from one sample weight sequentially by FAAS [12] or by ICP AES [13]. The matrix interferences are compensated by background correction and standard additions [19]. GF AAS is used to determine Al, As, Ca, Cd, B and Si mainly for lower trace concentrations. The multimethod analysis of reference steel samples by various instrumental methods (ICP AES, INAA, TXRF, ASS and DPASV) has been discussed [35].

Chromium improves corrosion resistance, high temperature strength of steel and ferroalloys and coercive forces in magnets and magnetic tapes. Chromium dissolves in HCl [23,24] or a mixture of HCl-HClO₄ [22]. Chromium (III) is oxidized to Cr(VI) by HClO₄ and trace elements can be separated by ion exchange on cellulose-Hyphan [23], or on cellulose loaded with In(OH)₃ [23], or by coprecipitation with La(OH)₃ [22].

Manganese matrix enjoys interest because of the utilization of Mn

nodules and adverse effects of the impurities in Mn alloys and Mn dioxide. Manganese is dissolved in HCl and cation exchange is preferred for the separation of impurities [25].

Cobalt-, Cr- and Ni-based alloys may require days for dissolution by conventional methods, but are easily dissolved in a few minutes with microwaves. The dissolution in HF-HNO₃ or *aqua regia* with HF and evaporation with H₂SO₄ and H₃PO₄ was efficient [36].

For the analysis of alloys containing high levels of W excessive heating with concentrated HNO₃ can lead to the precipitation of tungstic acid. They are dissolved in hot HCl-HNO₃ (4+1) followed by the addition of HF and evaporation to near dryness.

11.1.2 Non-ferrous metals and alloys

The most important materials of this group include high purity aluminium (reactor clads), copper (contacts and wires), Ga and In in semiconductors and Sn- and Pb-metals used for solders and batteries. Analysis of non-ferrous alloys has been reviewed [37]. Methods for multielement trace analyses are summarized in Table 11.2.

TABLE 11.2

Multielement trace analysis of non-ferrous metals, alloys and related compounds

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref
Aluminium (2 g)	HCl	sorption on cellulose with chelating agents	ICP AES, FAAS	Cr, Cu, Fe, Mn, Pb	38
Aluminium (2 g)	HCl	sorption on HMDTC loaded cellulose	TXRF	Bi, Co, Cu, Fe, Ni, Pb, U, V, Zn	39
Aluminium (6 g)	NaOH soln.	sorption of APDC complexes on charcoal	DCA AES	Co, Cu, Mn, Ni, Pb, Zn	40
Aluminium (0.1 g)	HCl-HF	removal of Na ⁺ on Sb ₂ O ₅ aq	RNAA	53 elements	41

continued

TABLE 11.2 (continuation)

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref
AlCl ₃ (20 ml)		sorption of DDTC complexes on C ₁₈	FAAS	Ag, Al, Cd, Cr, Fe, Mn, Ni, Pb	42
Al-alloys	n.g.	sorption on a chelating ion- exchanger	ICP AES	Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, Zn	43
Copper (5 g)	<i>aqua regia</i>	copptn. with In(OH) ₃	ICP AES	As, Bi, Pb, Se, Sn, Te	44
Copper (1–5 g)	HNO ₃	none	GFAAS	Ag, As, Bi, Cd, Co, Cr, Mn, Ni, Pb, Sb, Se, Sn, Te	45 46
Copper (0.4–2 g)	HNO ₃	anodic deposition of Pb; anion-exchange	ID TIMS	Cr, Ni, Zn, Cd, Pb	47
Copper, Cu oxide and alloys (1 g)	HCl–HNO ₃	none	ICP AES	Al, Fe, Zn, Pb, Ni, Sn Al	49
Copper, lead	HNO ₃ – tartaric acid	volatn. as hydrides	ICP AES	As, Sb, Sn, Bi, Se, Te	50
Copper (1 g)	HNO ₃	copptn. with La(OH) ₃	GF AAS	As, Bi, Cr, Fe, Pb, Sb, Se, Te	48
Cu-alloys (1 g)	HCl–H ₂ O ₂ – HNO ₃	pptn. of Cu as CuSCN; extrn. of Sn as SnBr ₄ ; copptn. with cellulose as HMDTC complexes	FAAS, GF AAS	Au, Bi, Cd, Co, Fe, Ga, In, Mo, Ni, Pb, Sb, Se, Sn, Zn	51
Lead (2 g)	HNO ₃	evapn. to dry- ness, leaching with EtOH	GF AAS	Ag, Cd, Cu, Fe	52
Pb–Sn alloys (1 g)	HNO ₃ –HF	none	ICP AES	Al, As, Sb, Bi, Cd, Cu, Au, Fe, Ni, Ag, Zn, Na	53

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref
Pb-Sb alloys (5 g)	HBr-Br ₂	matrix pptn. as bromide	FAAS	As, Bi, Cd, Co, Cr, Cu, Fe, In, Mn, Ni, Se, Tl, Zn.	54
Lead, Sn-alloys (0.4-1 g)	HBr-Br ₂	pptn. of Pb as PbSO ₄	FAAS	Ag, Bi, Cd, Fe, Ni, Cu, Zn	55
Lead, Pb-alloys (6 g)	HNO ₃	none	ICP AES	Ag, As, Bi, Cd, Cu, Fe, Cd, Mn, Ni	56
Tin (0.1 g)	HBr-Br ₂	none	GF AAS	Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Sr, V, Yb	57
Gallium (1 g)	HCl (gas)	volatn. as GaCl ₃ ; residue dissolved in HNO ₃	GF AAS	Al, Cd, Cu, Fe, Mg, Pb	58
Gallium (1 g)	HCl-HNO ₃	controlled dissolution	ICP AES, GF AAS	Ag, Bi, Cu, Fe, Ni, Pb	59
Gallium (1 g)	HCl	extrn. of GaCl ₄ (MIBK)	ICP AES GF AAS	Al, Ca, Cd, Co, Cu, Mg, Mn, Ni,,Pb, V, Zn	59
Gallium (n.g)	HCl-HNO ₃ (bomb)	extrn. with APDC	GF AAS	Cd, Co, Cu, Fe, Ni	60
Gallium (0.6 g)	n.g.	extrn. with DOTC		Bi, Ca, Cd, Cu, Fe, Mn, Mo, Ni, Pb, Si, Sn, Te, Zn	61
Gallium (1 g)	HCl-HNO ₃	extrn. of Ga with β,β'-dichloro- diethylether	GF AAS	23 elements	57
Indium (1 g)	HBr	extrn. of In with β,β'-dichloro- diethylether	GF AAS	21 elements	57

continued

TABLE 11.2 (continuation)

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref
Indium (1–2 g)	HNO ₃	none	FAAS	Ag, Al, Bi, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sb, Te, Tl, Zn	56
Indium (0.2 g)	HNO ₃ –HF	extrn. chromatography with TBP from 6 M HBr	RNAA	22 elements	62
Indium (1–2 g)	HNO ₃	none	GF AAS	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Tl, Zn	56
Indium (1–2 g)	HNO ₃	volatn. as hydrides	QF AAS	As, Bi, Hg, Sb, Sn, Se, Te	63
La nitrate	H ₂ O	none	GF AAS	Co, Cu, Fe, Ni, Cu	64
REE compounds	HCl	none	FAAS, ICP AES	Ca, Fe, K, Mg, Na	65

Aluminium and Al alloys are dissolved in concentrated HCl in the presence of H₂O₂ [38,39]. Upon simple dilution the solution can be analyzed for Cu, Fe, Mg, Mn, Ni, and Zn by FAAS. The aspecific absorption produced by the Al matrix requires Smith–Hieftje or Zeeman background correction in GF AAS. The refractory character of the Al prevents the analytes from being efficiently atomized, because of occlusion or formation of intermetallic compounds. The effects are alleviated by matrix modification with conc. HNO₃ with addition of LaCl₃ which acts as releasing agent or doping the Ar atmosphere with CHCl₃. The addition of NH₄F to the solution is effective except in the AlF absorption spectrum zone (peak at 227.5 nm). The Al matrix can be removed by precipitation as AlCl₃·6H₂O [66] or, alternatively, traces can be preconcentrated by ion exchange [43] or sorption on cellulose [38,39,67] or charcoal [40] collectors with different chelating agents.

High purity aluminium can be readily analyzed by INAA. After a few minutes decay, all the residual activity is due to impurities apart from ^{24}Na produced by the $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$ reaction [68].

Copper and Cu alloys are commonly analyzed for Al, Sb, As, Cu, Fe, Pb, Mn, Ni, Si, Sn and Zn. High purity copper is dissolved in concentrated HNO_3 [45–47]. Dissolution of Cu alloys is hampered by the precipitation of Sn as metastannic acid when HNO_3 is used and by that of PbCl_2 when HCl is used. A HCl-HNO_3 mixture is recommended provided that the final solution is not allowed to stand for long periods and the HCl strength is maintained when the solutions are diluted. Dissolution of Cu alloys in pressurized sample preparation devices has been studied [69]. They are readily dissolved in $\text{HNO}_3\text{-HCl}$ but if W, Ti or Nb are present the use of the $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ mixture is necessary. Copper has a rich ICP emission spectrum so a careful line selection is necessary [49]. In AAS the aspiration of concentrated Cu solutions may lead to the formation of explosive Cu acetylide in the nebulizer [70]. Many traces can be separated by coprecipitation as hydroxides with NH_3aq in which Cu forms a soluble stable $\text{Cu}(\text{NH}_3)_4^{2+}$ complex [44].

With regard to *lead, tin and related alloys*, some trace impurities (e.g. As, Te, Se) in Pb and Pb alloys (Pb–Sb, Pb–Ca–Al, Pb–Ca–Sn–Al) lower the hydrogen overpotential and may cause gassing problems during battery charging [56]. Lead- and tin-based solders contain 0.1–99% Pb, 0.595% Sn and 0.02–20% Sb and small or trace elements of other metals (e.g. Ag, Bi, Cd, Cu, Fe, Ni, Zn). Lead is not dissolved in H_2SO_4 because an insoluble PbSO_4 coating form. Solders dissolve in $\text{HNO}_3\text{-HF}$ mixture or *aqua regia* with some limitations. Tin and Sb may precipitate as metastannic and metastibonic acids, respectively. Traces of Sn in lead matrix can be successfully determined on dissolution in HNO_3 but the Sb present needs to be complexed by addition of NH_4F . Other methods use a mixture of HBr and Br_2 [55]. Lead precipitates as PbOF_2 in the presence of fluoride; HBF_4 is used to prevent this process. The lead can be separated as PbSO_4 or PbCl_2 or complexed with tartrate or EDTA. Coprecipitation of traces on PbSO_4 has been discussed [55].

Zinc and Zn-base alloys are analyzed for Pb, Fe, Mn, Al, Cd, Cu. They are readily dissolved in HCl with addition of H_2O_2 or HNO_3 . No particular dissolution problems occur.

Gallium is a basic material for the production of GaAs and GaP semiconductors. Metallic gallium dissolves in a mixture of HCl-HNO_3 (3+1). Direct GF AAS calibrated with electrolytically spiked standards

has been proposed [71] but it suffers from signal suppression [59]. The gallium matrix can be extracted as GaCl_4^- [59], with ethylhexylphosphoric acid [59] or with β,β' -dichlorodiethyl ether [57]. Trace impurities can be preconcentrated through controlled dissolution or extraction with APDC [59]. Different multistep analytical procedures have been compared with direct analysis by SS MS and GD MS [59].

Indium has similar applications to gallium. The metal dissolves readily in HBr [57] and in HNO_3 [56]. The solution can be analyzed directly by FAAS or GF AAS [56]. Indium can be separated by extraction with β,β' -dichlorodiethyl ether [57] or extraction chromatography with TBP from HBr media [62].

11.1.3 Refractory metals and alloys

Tungsten, Mo, Ta and Re metals are widely used (usually as sputter targets) for the production of metallization layers, metalloceramics and high-temperature alloys. Their characterization in terms of trace element impurities at 1–100 ppm and often lower levels is required. Not less stringent specifications are demanded for starting materials for the production of high purity metals, e.g. W or Mo-oxides or ammonium perrenate.

High performance analytical characterization of refractory metals has been reviewed [72]. Direct methods (GD MS, SS MS and SI MS) enjoy increasing interest albeit they suffer from low sample volume consumed and imprecisions in bulk analysis [73]. Oxides are readily dissolved in alkalis [74] or can be analyzed as slurries (e.g. MoO_3 by ETA AAS) [75]. Pure metals are difficult to dissolve. Direct ICP AES analysis of solutions is hampered by line rich spectra and 1% salt tolerance which adversely affect the detection limits achieved. The higher sensitivity of ICP MS is offset by strong matrix suppression and hence only 0.001% concentration is allowed. AAS methods are favoured because of higher selectivity but FAAS is too insensitive whereas GF AAS is prone to interferences. Direct XRF is not feasible because of high absorption of refractory matrices. INAA has limited potential but RNAA offers very low detection limits and high accuracy [75] but small portions and short irradiation are required which affect the limit of detection [76]. All these reasons favour wet combined procedures especially for the ng/g range of concentrations. Hydrogen peroxide is frequently added to retain these metals in solution. Trace contents of elements in doubly purified H_2O_2 have been listed [77]. Cellulose collectors, untreated or

modified with chelating groups are efficient for multielement trace precipitation [24]. Analytical methods are summarized in Table 11.3.

TABLE 11.3

Multielement trace analysis of refractory metals, alloys and related compounds

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Tantalum (0.1 g)	HF-HNO ₃	none	ICP MS	V, Cr, Ni, Co, Cu, Zn, Zr, Cd, Hg, Pb, U	78
Tantalum (1 g)	HF-HNO ₃	cation-exchange	ICP AES	Ag, Ba, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Ni, Pb, Sr, Tl, Zn	78 79
Tantalum	HF-HNO ₃	extrn. of Ta with DAM (C ₂ H ₄ Cl ₂), anion-exchange	ICP AES	35 elements	80
Molybdenum (1 g)	HNO ₃ -HCl	copptn. with La(OH) ₃ , volatn. as hydrides	ICP AES	As, Bi, Sb, Se, Te	81
Molybdenum (1 g)	HNO ₃ -HCl	copptn. with La(OH) ₃	ICP AES	Co, Cr, Cu, Fe, Mn, Ni, Ti, V, Zn, Zr.	74
MoO ₃ -powder	NaOH	copptn. with La(OH) ₃	ICP AES	Co, Cr, Cu, Fe, Mn, Ni, Ti, V, Zn, Zr	74
Molybdates (4 g)	ascorbic acid soln.	extrn. with 2-(2- benzoxazoylyl)- malonaldehyde (MIBK)	FAAS	Cd, Co, Cu, Fe, Mn, Ni, Zn	82
Molybdenum, tungsten	HF-HNO ₃ , NaOH	cellulose Hyphan	ICP AES	Al, Ca, Co, Cu, Fe, La, Mg, Mn, Nb, Ni, Ta, Th, Ti, U, Y, Zr	24
Molybdenum (0.1 g)	HF-HNO ₃	anion-exchange	RNAA	20 elements	83

continued

TABLE 11.3 (*continuation*)

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Molybdenum, tungsten, MoO ₃ , WO ₃ powders (1 g)	H ₂ O ₂	cation-exchange	ICP AES	21 elements	77
Molybdenum, tungsten (up to 4 g)	H ₂ O ₂ or HF-HNO ₃	cation-exchange	ID TIMS	Ca, Cd, Cr, Cu, Fe, Ni, Th, U	84
Mo,W,Ta-silicides niobium, quartz	HF-HNO ₃	cation-exchange	ID TIMS	Ca, Cd, Cr, Cu, Fe, Th, U	85
Tungsten (1 g)	HF-HNO ₃	none	FAAS	K, Fe, Ni	86
Tungsten (1 g)	HF-HNO ₃	none	ICP AES AAS	25 elements	87
Tungsten (0.5 g)	HF-HNO ₃	none	ICP AES	27 elements	88
WO ₃ -powder (0.01-0.1 g)	NH ₃ aq	sorption on TMDTC-loaded activated carbon	GF AAS	Bi, Sb, Sn	89
WF ₆ (ng)	evapn.; dissoln. in NH ₃ (aq)	none	ICP MS	As, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Th, U	90
Ammonium perhenate (0.5 g)	H ₂ O	extrn. with DDTC-TMDTC	FAAS GF AAS	25 elements	91
Rhenium	H ₂ O ₂ or HNO ₃	extrn. of Re with tri- <i>n</i> -octylamine oxide (toluene)	GF AAS	Bi, Cd, Cr, Ni, Pb	57
Titanium (0.3-2.2 g)	HF	cation-exchange	ID TIMS	Cd, Cr, Cu, Fe, Ni, Pb, Th, U	92
Titanium (1 g)	HF-HNO ₃	Chelex 100 or cellulose Hyphan with HN DDTC	CP AES	17 elements	93
Titanium	HF-HNO ₃	none	ICP MS	Ba, Ce, Cr, Cu, Fe, Ni, Pb	94

Tantalum dissolves in a mixture of HF-HNO₃ [78–80]. The limitations of ICP AES and ICP MS have been evaluated [78]. Direct analysis offers detection limits of 0.1–10 ppm for alkali earth and transition metals whereas ppb levels can be reached only after wet-chemical preconcentration procedure [79]. Tantalum matrix can be separated by extraction with diantipyrilmethane from 12 M HF [80] or by ion exchange [78].

Molybdenum dissolves in HNO₃-HCl [74,81] and can be analyzed directly by ICP AES [24,77]. A chemical separation, e.g. by coprecipitation of the impurities with La(OH)₃ [74,81], or by ion exchange [95], is necessary to minimize the matrix effect and to concentrate analytes. A radiochemical separation scheme for multielement analysis of high purity molybdenum has been developed [83].

Tungsten dissolves in HF-HNO₃ whereas its oxide (WO₃) is readily dissolved with H₂O₂. HF is the only acid to dissolve tungsten; the removal of the fluoride causes precipitation of H₂WO₄ [86]. Direct analysis by SI MS has been discussed [96]. Graphite furnace AAS cannot be used in the presence of W matrix because of the formation of W carbide [89]. Direct ICP AES requires a careful line selection [88,97] while ICP MS needs a drastic dilution of the solution fed [98]. Various sample handling techniques for GF AAS [89] have been compared. Tungsten can be volatilized as WF₆, precipitated as the cupferronate, extracted with TOA or a quaternary ammonium salt or separated by ion chromatography [98]. The disadvantage of volatilization is the possibility of losses of CrO₂F₂ and UF₆ [98].

Rhenium can be analyzed directly by GF AAS on fractional evaporation of impurities in the furnace at the expense of strong signal suppression [57]. The matrix can be separated by extraction with tri-*n*-octylamine oxide to improve the detection limits [57]. Sodium, K, Ca, Mg and Si can be determined directly in the presence of a Re matrix by FAAS.

Titanium is readily dissolved in HF-containing oxidizing acids [92]. Removal of the Ti matrix by 1 decade improves detection limits in ICP AES by 2–3 decades [93].

11.1.4 Precious metals

The precious metals include silver, gold and Pt group metals, used usually in electronics. Analytical methods are summarized in Table 11.4.

TABLE 11.4

Multielement trace analysis of precious metals

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Silver (0.5 g)	HNO ₃	extrn. of Ag with <i>O</i> -isopropyl- <i>N</i> -methylthiocarbamate	GF AAS	As, Bi, Cd, Pb, Sb, Se, Te	57
Silver (0.1 g)	HNO ₃	none	GF AAS	Bi, Cu, Fe, Ni, Pb, Se, Te, Zn	70
Native silver artefacts (0.5 mg)	HNO ₃	none	ICP MS	As, Bi, Co, Cu, Hg, Ni, Pb, Sn, Sb, Te, W, Zn	99
Gold (0.5 g)	<i>aqua regia</i>	extrn. as AuCl ₄ ⁻ (MEK/CHCl ₃)	FAAS, GF AAS	20 elements	100
Gold (0.25 g)	<i>aqua regia</i>	pptn. with N ₂ H ₄	GF AAS	As, Sb, Sn	101
Gold (1–10 g)	HNO ₃ –H ₂ SO ₄ –H ₂ O ₂	extrn. of Au with <i>n</i> -Bu ₂ S	GF AAS	Ag, As, Bi, Cd, Pb, Pt, Se, Te	57
Gold (6 g)	<i>aqua regia</i>	none	ICP AES	Fe, Cu, Pd	102
Pd compounds (1 g)	HNO ₃	none	ICP AES	Ag, Au, Cu, Fe, Ni, Pt, Zn	103
Platinum (0.2 g)	HCl–HNO ₃	EtOH enhanced nebulization	FAAS	Ag, Bi, Cd, Co, Pt	104
Platinum (2 g)	<i>aqua regia</i>	extrn of PtCl ₆ ²⁻ (MIBK- <i>i</i> -PeOH)	FAAS	Al, Ca, Cr, Cu, Mg, Mn, Ni, Pb	105
Platinum, palladium (0.2 g)	Pd: HNO ₃ Pt: <i>aqua regia</i>	none	GF AAS	Ag, Cd, Co, Fe, Ir, Ni, Mn, Pb, Rh, Ru	106
Platinum (0.1–1 g)	<i>aqua regia</i> (bomb, microwave assisted)	none	GF AAS	Au, Pd, Pb	34

Silver dissolves readily in HNO_3 . Aspiration of concentrated Ag solutions may lead to the formation of explosive Ag acetylide in the nebulizer [70]. The silver matrix can be separated by extraction into MIBK from iodide media or AgCl precipitation [70] or extracted with *O*-isopropyl-*N*-methyldithiocarbamate [57]. Analysis of silver by ETA AAS has been discussed [57].

Gold is dissolved in *aqua regia* to give the AuCl_4^- complex. To bring Rh and Ir completely into solution electrolytic dissolution of gold may be necessary [57]. The gold matrix can be extracted as a halide complex into *O*- or *S*-containing organic solvents, e.g. ketones [100] or di-*n*-butyl-sulphide, or into CHCl_3 [57] or removed by precipitation after reduction to Au^0 , e.g. by hydrazine [101]. Direct analysis of gold for Pd, Fe, Cu has been evaluated [102]. Analysis of gold by ETA AAS has been discussed [57].

Dissolution of *platinum group metals* was discussed [107]. Pure platinum is difficult to dissolve. Up to 3 days heating with *aqua regia* are required. Dissolution of Pd is easier. The matrix can be extracted as chloride complexes [105]. Rhodium dissolves in hot H_2SO_4 and HBr. Iridium powder is dissolved in HCl in the presence of an oxidant, e.g. KClO_3 when heated at 300°C in a Carius tube. Finely divided osmium and ruthenium dissolve in alkaline hypochlorite solutions. Fusion with oxidizing fluxes is a valid alternative for all the platinum group metals.

11.2 SEMICONDUCTING MATERIALS AND RELATED PRODUCTS

The electronics industry makes use of high and ultrahigh purity materials which must be strictly defined in terms of impurities contents (often in the ng/g and lower range). They include high purity metalloids (Si, Ge, Se, Te), quartz, $\text{A}^{\text{III}}\text{B}^{\text{V}}$ compounds (where A denotes Ga, In and B denotes As, Sb, P) and $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ compounds (A = Zn, Cd, Hg; B = Se, Te), and materials used for their manufacturing (photoresists and high purity gases and reagents). Analytical chemistry of electronic materials has been reviewed [3]. Selected analytical methods are summarized in Table 11.5.

11.2.1 Semiconducting materials

The analytical characterization of semiconducting materials must include the determination of the bulk level of traces and/or the spatial distribution of the dopant elements. The latter requires layer-by-layer

TABLE 11.5

Multielement trace analysis of electronic materials

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Silicon (0.5 g)	HNO ₃ -HF	volatn. of SiF ₄ in the presence of mannitol	ICP AES	B, Cr, Cu, Mn, Ni	108
Silicon, silica	HNO ₃ -HF	volatn. as SiF ₄	TXRF	31 elements	109
Silica (1 g)	HNO ₃ , HCl, HF (bomb)	none	FAAS	Al, Ca, Cu, Fe, Mg, Mn, Na, Ti	110
Selenium (0.5 g)	HNO ₃	redn. pptn. with hydrazine	GF AAS	As, Sb, Sn	111
Selenium (0.5-5 g)	HNO ₃	extrn. of Se as SeO ₂	FAAS	Ag, Au, Ca, Cd, Cu, Mg, Mn, Ni, Pb, Sb, Te, Zn	112
Selenium (1-5 g)	HNO ₃	sorption as PMBP or DDTC complexes on activated carbon	FAAS	Bi, Cd, Co, Cu, Fe, Mn, Pb, Te, Zn	113
Tellurium (1.25 g)	HCl-HNO ₃	none	GF AAS	24 elements	114
Arsenic (0.2 g)	HCl-HNO ₃	none	GF AAS	Ag, Al, Ca, Cr, Cd, Co, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sr, Sn	57
Arsenic (2 g)	HNO ₃ -HCl	none	GF AAS	Ag, Al, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Tl, Zn	115
Gallium arsenide (0.015-0.04 g)	HNO ₃ -HCl	none	GF AAS	Mg, Si, Zn	116-118

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements determined	Ref.
Gallium arsenide (1 g)	HCl-Br ₂	volatn. as chloride/bromide	GF AAS	Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn	119
Gallium arsenide (0.01 mg)	none	volatn. in an Ar-Cl ₂ stream	GF AAS	Mn, Ag, Bi, In, Pb	120
Gallium arsenide (0.5 g)		volatn. as bromide	GF AAS	Fe, Ca, Mg, Ni, Cu, Al, Pb, Co, Mn, Cr	121
Indium arsenide	HBr-HNO ₃	none	GF AAS	Ag, Au, Bi, Cd, Ge, Sn, Tl	122 123
Indium phosphoride (1 g)	HCl, HNO ₃	none		Ag, Al, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Si, Sn	124
Copper indium sulphide (50-100 mg)	HNO ₃ (bomb)	electrodeposition of Cu; extrn. as chloride complexes (DIPE)	AAS	Fe, Ga, Tl	125
Trimethyl- gallium (8.6 ml)	HCl	extrn. of as GaCl ₄ ⁻ (DIPE)	GF AAS	Al, Ca, Cd, Co, Cr, Cu, Mg, Mn, Ni, Pb, Ti, V, Zn	126
Trimethyl- gallium (1 g)	HCl	none	ICP AES	Al, Cu, Fe, Mg	127
Trimethyl- aluminium	EtOH	residue digested with H ₂ O ₂	ICP AES	Cu, Fe, Ga, Mg, Si, Zn	128
Negative photoresist	dil. with Shell-Solv 70	none	ICP AES	Al, B, Ca, Cu, Fe, Mg, Ni, Si, Y, Zn	129
Negative photoresist	dil. with xylene	none	GF AAS	K, Na, Sn	129

PMBP: 1-phenyl-3-methyl-4-benzoyl-5-pyrazol-3-one.

sampling methods which include mechanical separation by a diamond knife microtome (depth resolution 1–2 μm), chemical etching (depth resolution 0.1–1 μm) or chemical etching after anodic oxidation (depth resolution 0.01–1 μm) [130]. The first procedure leads to microamounts of powder of the separated sample, which can be weighed and dissolved. The second and third procedures lead to microvolumes of dissolved samples. Methods for dissolution of various samples have been discussed [131]. Analytical chemistry of semiconducting materials was reviewed [132,133] with particular emphasis on NAA [131,134] and ICP AES [135].

Solid sampling avoids time-consuming dissolution, digestion, preconcentration steps and nebulization losses and has the further advantage of reducing dangers of contamination and increasing the sensitivity and lowering the detection limit of the particular element to be determined. Unfortunately there are several disadvantages associated with solid sampling, e.g. the small masses involved (0.1–1 g) may not be representative of the whole sample owing to inhomogeneity problems, transfer to the furnace or plasma may lead to imprecision, calibration standards are difficult to obtain and there may be an increase of interference effects. A number of AAS and ICP AES methods have been reported for the determination of trace elements in semiconductor materials. As they are principally solution based techniques, dissolution of the semiconductor material is normally required.

Silicon and quartz

For individual wafers, which contain only a few milligrams of amorphous silicon, microanalytical techniques are required. An extensive multimethod comparison study for quartz has been published [136]. Neutron activation is particularly suitable for the analysis of silicon as the γ -activity of the ^{31}Si produced during irradiation of the sample is relatively low and its half-life is only 2.62 h [132–134,137]. Vapour phase decomposition of high purity quartz has been developed; ICP AES [108] and TXRF [109] are suitable detection techniques after matrix removal by volatilization.

Germanium

It is possible to separate thin (down to 1 μm) germanium layers in the form of powder using diamond knife in the microtome. For thinner layers chemical etching by HF-HNO_3 was used. For layer-by-layer analysis it was necessary to wash the surface of the Ge sample with a

mixture of HCl-HNO₃ between etching to avoid hydrolysis of Geⁿ⁺ substances to gelatinous GeO₂aq [130].

Selenium

Dissolution of high-purity selenium in HNO₃ yields hardly soluble metastibonic and metastannic acids [111–113]. Citric acid is the most suitable complexing agent to keep Sb and Sn in solution. The selenium matrix is removed by reductive precipitation with hydrazine [111] or extraction as SeO₂ into *n*-butanol [112]. Ion-exchange and extraction methods are not applicable for separation of As, Sb and Sn from Se matrix owing to their close ion-exchange properties and volatility.

Tellurium

Tellurium multielement analysis by SS MS, GD MS and GF AAS has been discussed [114].

A^{III}B^V compounds

Thin (>1 μm) layers of A^{III}B^V compounds can be separated as powders using a diamond knife in the microtome. For thinner layers chemical etching by CH₃OH/Br₂ or by HF after anodic oxidation has to be used [130]. Decomposition of these materials involves etching (H₂SO₄-H₂O₂) to remove surface contamination followed by dissolution in HNO₃ or HCl-HNO₃. For the determination of Ag, Au, Cd and Sn in indium arsenide chemical etching with HBr-HNO₃ has been used [130]. Neutron activation analysis of gallium arsenide is inconvenient since two nuclides with high activities, ⁷²Ga (*t*_{1/2} = 14.1 h) and ⁷⁶As (*t*_{1/2} = 26.4 h) are produced from the matrix and need to be separated. Analysis of gallium arsenide by GF AAS is affected by the molecular absorption of GaCl and GaO in the 225–275 region [116,117]. Use of NH₄Cl as a matrix modifier has been proposed [119]. An alternative is volatilization of As in the stream of Ar-gas and of Ga in the presence of chloride [120]. A direct method for InP-crystal multielement analysis has been developed but all the impurities were below detection limits [138].

Other compounds

Copper indium disulphide (CuInS₂) is only sparingly soluble in HCl-HNO₃-HF but is readily decomposed by HNO₃ in a pressure bomb [125]. Cadmium mercury telluride (Cd_xHg_{1-x}Te, where *x* = 0.1 – 0.3) dissolves readily in concentrated H₂SO₄.

11.2.2 Electronic grade gases and chemicals

Hydrides and alkyls of III–VI group elements are used as starting materials for the production of semiconductor thin layers. The gases, silane (SiH_4), trichlorosilane (SiHCl_3), trimethylgallium and trimethylaluminium, are highly pyrophoric and thus require highly specialised techniques and safety precautions. They cannot be analyzed directly by neither INAA or ICP AES because of low boiling point and radiolysis products [97] and are usually decomposed prior to analysis in HCl [126,127] or EtOH [128]. The direct analysis of silane by ICP MS at the sub-ppb level has been reported [139].

Electronic grade auxiliary materials include ammonia, hydrogen peroxide, and sulphuric and phosphoric acids. They can be analyzed using quadrupole ICP MS to the levels currently required for the industry [140]. For customized oligoelement analysis GF AAS is the method of choice [141]. Analysis of high purity acids by TXRF has been discussed [142,143].

Photoresists are dissolved in organic solvents and fed into the ICP for multielement analysis [129].

11.3 ANALYSIS OF CERAMICS AND THEIR BASIC PRODUCTS

The diversity in chemical composition of the materials to be analyzed is very large. Generally ceramics consist of oxides (such as Al_2O_3 , ZrO_2 , TiO_2) which have high melting points and low solubility but nitrides (AlN , ZrN) and carbides (SiC) are becoming increasingly popular. Trace elements influence mechanical stability, radiation and thermal stability, conductivity, semiconductor properties and superconductivity. The requirements apply both to sinter product and basic components. Analysis of advanced ceramics and their basic products has been reviewed [144,145] with particular emphasis on ICP AES [146] and AAS [147].

11.3.1 General analytical approaches

Sampling

Most commercial ceramics are available as homogeneous powders. If not, after cleaning, sample crushing and grinding can be accomplished choosing mortars depending on the type of contamination that can be tolerated. Samples should not be ground any finer than is necessary for

subsequent decomposition. Most acid and fusion decompositions require size reduction to less than 100 mesh but some fusions of extremely refractories need 200 mesh. Abrasion, up to 0.025% from WC mills is common and W is a common interferent [145]. Some reduction in particle size is often necessary to render the sample suitable for digestion.

Direct analysis

Slurry nebulization ICP AES is the preferred option if a powder is already available but can be applied only if the particle size of the powder is below a certain limit [66,148–152]. Direct insertion of small powder amounts into the ICP was proposed [153]. INAA is particularly suitable for Al and Si based ceramics [144,145]. The sensitivity of XRF is restricted to the ppm level and light elements cannot generally be measured. The effect of colloidal stability of ceramic suspensions on nebulization of slurries for ICP AES has been studied [154]. Hydrocarbon assisted slurry vaporization for ICP AES of Si_3N_4 has been proposed [155].

Decomposition

Ceramic powders are very resistant and require highly aggressive reagents and conditions. Most oxidic materials cannot be completely dissolved by acids. Acid digestion in pressure bomb (also microwave-assisted [156]) is preferred to fusion because of the risk of contamination and lower salt content. The complexing effect of HF is pronounced in pressure decompositions of resistant oxides of the elements that form stable complexes with fluoride. The data published on the decomposition of oxides are not always complete and lack the thermal history and the crystal structure of the compound. The speed of the dissolution depends on the specific surface area, the grain size, the phase state, and the purity. Ignited oxides and single crystals are highly resistant toward acids even in the pressure decomposition.

Combined procedures

Separation methods are based either on matrix removal and multielement trace analysis of the residue or on the group extraction (or coprecipitation) of the desired analytes. ICP AES and ICP MS are the preferred determination techniques. GF AAS is efficient but time consuming and prone to a variety of errors. Analytical methods involving a chemical preparation step are summarized in Table 11.6.

TABLE 11.6

Multielement trace analysis of advanced ceramics

Sample	Decomposition	Separation/ preconcentration	Detection	Elements determined	Ref.
Alumina	HCl-H ₂ SO ₄ (bomb)	pptn. as AlCl ₃	GF AAS	Al, B, Ca, Co, Cu, Fe, Mg, Mn, Si, Ti, W, V, Zn	66
α-alumina (0.5 g)	H ₃ PO ₄ or H ₃ PO ₄ - H ₂ SO ₄		ICP AES	Ca, Cr, Cu, Fe, Ge, Li, Mn, Na, Si, Ti	157
Alumina (5 g)	HCl-HF (bomb, microwave), HClO ₄ , HNO ₃ -HCl	none	ICP MS	Ba, Ce, Fe, Ni, Pd, Rh	158
Alumina (0.1 g)	HCl-H ₂ SO ₄ (bomb, microwave)	none	MIP AES	Ca, Cu, Fe, Mg, Na, Zn	156
Alumina (1 g)	HCl-H ₂ SO ₄ (bomb)		ICP MS	B, Ba, Ca, Ce, Cr, Co, Cu, Fe, Ga, La, Na, Mg, Mn, Ni, Zn, Zr	159
Alumina, aluminium nitride (0.1-0.15 g)	HCl (bomb)	removal of ²⁴ Na on Sb ₂ O ₅	RNAA	56 elements	160
CrSi ₂ (1 g)	HNO ₃ -HF- HClO ₄	copptn. with La(OH) ₃ after oxidn. of Cr to Cr(VI)	ICP AES	As, Co, Cu, Fe, In, Mn, Ni, Ti, V, Zn, Zr	22
Eu ₂ O ₃		extrn. with DDTC	FAAS, GF AAS	Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	161
ZrSi ₂ , ZrB ₂ (0.25 g)	HF-H ₂ SO ₄ , H ₂ SO ₄ (bomb)	none	ICP AES	Al, Ca, Co, Cr, Fe, Hf, Mg, Mn, Ni, Sr, Ti, V, W, Y	162

Sample	Decomposition	Separation/ preconcentration	Detection	Elements determined	Ref.
ZrC-, ZrN- powders (0.5 g)	HNO ₃ -HF (bomb)	none	ICP AES	Al, Ca, Co, Cr, Fe, Hf, Mg, Mn, Mo, Na, Nb, Ni, Si, Ti, V, W	163
ZrO ₂ -powder (0.1 g)	fusion with NH ₄ HSO ₄	matrix removal with TTA	ICP AES	Al, B, Ca, Cu, Fe, Mg, Mn, Na, Ti, V, Y	147
ZrO ₂ -powder (0.3–0.4 g)	H ₂ SO ₄ (bomb)	none	ICP AES	Al, B, Ca, Cu, Fe, Mg, Mn, Na, Ti, V, Y	147
Aluminium nitride, zirconia (0.2 g)	fusion: Na ₂ CO ₃ – Na ₂ B ₄ O ₇ or dissoln.; H ₂ SO ₄ – (NH ₄) ₂ SO ₄ or HCl (bomb)	none	ICP AES	Al, Ca, Fe, Mg, P, Si, Ti	165
Aluminium nitride (0.1 g)	HNO ₃ (bomb, microwave assisted)	none	MIP AES	Ca, Cu, Fe, Mg, Na, Zn	156
Barium titanate (0.5 g)	HCl (bomb)		ICP AES	Al, Ca, Cu, Fe, Hf, Mg, Na, Nb, Ni, Si, Sr, Zr	166
Barium titanate (0.2 g)	HCl or fusion (Na ₂ CO ₃ or Li ₂ B ₄ O ₇)	none	ICP AES	Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Na, Nb, Ni, P, Pb, Si, Sr, W, Zn, Zr	167
Titanium carbide, titanium nitride (0.5 g)	HNO ₃ -HF	none	ICP AES	Al, Ca, Co, Cr, Fe, Mg, Mn, Mo, Na, Nb, Ni, Si, V, W, Zn	168
Silicon nitride	volatn. of Si as SiF ₄	none	ICP AES	Al, B, Ca, Co, Cu, Fe, Mg, Mn, Si, Ti, W, V, Zn	66

continued

TABLE 11.6 (*continuation*)

Sample	Decomposition	Separation/ preconcentration	Detection	Elements determined	Ref.
Boron nitride, silicon nitride (0.1 g)	HF-H ₂ O ₂	none	MIP AES	Al, Ca, Cu, Fe, Mg, Na, Zn	156
Silicon carbide (1 g)	HF-HNO ₃ - H ₂ SO ₄ (bomb)	none	ICP AES	53 elements	169
Silicon carbide (0.25 g)	HNO ₃ -H ₂ SO ₄ (bomb)	none	ICP AES GF AAS	Al, B, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Ti, V, Zn	170
Silicon carbide (0.25 g)	HNO ₃ -H ₂ SO ₄ - HF	complexn. with HMDDTC	ICP MS	Co, Cu, Cr, Fe, Ga, Mn, Ni, V	159
Superconducting materials			ICP AES	Fe, Gd, K, La, Mg, Na, Sn, Tm	171
Optical glasses (5 g)	HF-HNO ₃	copptn. with DDTC with Mo as collector	FAAS, HG AAS GF AAS	Ag, Bi, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, Pd, Tl, Zn	172
Monocrystalline SiC (1g)	HF-HNO ₃ (bomb)	none	ICP MS	Al, Cr, Cu, Mg, Mn, Ti, V, Zn	173

11.3.2 Industrial ceramics

Alumina and Aluminium nitride-based ceramics

Methods for their decomposition have been summarized [156]. The decomposition conditions are strongly dependent on the allotropic form. Whereas α -Al₂O₃ is highly resistant toward HCl vapours the γ -form of the oxide can be quantitatively dissolved. Attack with HCl under pressure at 200°C for a few hours is necessary [66]. Dissolution in polyphosphoric acids has found a wide application in analyses of all the crystal modifications of Al₂O₃ [174]. Corundum resists acids even in hot concentrated H₂SO₄ or H₃PO₄ and many fusion agents but can be dissolved by a melt of disulphate or KHF₂. α -Alumina dissolution has been discussed

[174]. Microwave-assisted digestion of alumina samples with various physico-chemical properties in H_2SO_4 (1+1) has been investigated [175]. A $\text{HCl-H}_2\text{SO}_4$ mixture was also found to be applicable to the sintered ceramics with grain size <2 mm but longer dissolution is required [66]. Aluminium nitride is dissolved in a HCl-HNO_3 mixture [66]. The Al matrix can be fairly easily removed by precipitation with saturated HCl as the crystalline hydrated AlCl_3 [66]. Alternatively, extraction of dithiocarbamates of transition metals or their coprecipitation on cellulose have been reported [67]. Alumina-based ceramic materials are readily analyzed directly by INAA [66] or ICP AES with external electrothermal vaporization [176] or a slurry technique [66].

Silicon carbide and nitride ceramics

Methods for the dissolution of boron nitride and silicon nitride were discussed [156]. Silicon nitride is decomposed with HF-HNO_3 [66,176] whereas for SiC a mixture $\text{HF-H}_2\text{SO}_4\text{-HNO}_3$ was used [66]. Silicon carbide powder could be completely dissolved in $\text{HNO}_3\text{-HF}$ and fuming H_2SO_4 in an autoclave at 240°C within 8–20 h. Fusion with alkaline oxidative mixtures is the most widely used method. The silicon matrix is volatilized in the presence of HF and HClO_4 . After matrix removal the residue is analyzed by ICP AES or GF AAS [177]. Silicon-based ceramics are readily analyzed directly by INAA or as slurry by TXRF or ICP AES [66]. ETV ICP AES analysis of silicon carbide for Ca, Fe and Ti has been reported [178]. An excellent multimethod comparison study has been published [66].

Titanium-based ceramics

Titanium carbide (TiC) and titanium nitride (TiN) are compounds with corrosion resistance, high hardness and refractory nature. Titanium carbide is attacked by HNO_3 , *aqua regia*, $\text{HNO}_3\text{-HF}$ and the nitride by boiling *aqua regia*. The $\text{HNO}_3\text{-HF}$ mixture is the most efficient. A robotic microwave digestion system for dissolution of titanium dioxide has been developed. It weighs out samples, adds acids, carries out microwave digestion, dilutes the solutions, transfers the solutions to beakers and cleans the digestion vessels [179].

Zirconium dioxide, nitride and carbide based ceramics

These are stabilized with Y_2O_3 , CaO or MgO , sometimes CeO_2 . Slurry ICP AES has been proposed [151]. Zirconia can be dissolved in a pressure bomb by H_2SO_4 (1+1) alone, HF or their mixture. An attractive

alternative is fusion with NH_4HSO_4 which is available at high purity [164]. Zirconium gives a line-rich ICP AES spectrum and GF AAS is hampered by the formation of refractory carbides. Matrix removal by extraction with TTA or precipitation as ZrOCl_2 has been proposed. The presence of NH_4F helped to remove severe matrix effects in the Zr matrix analysis [180].

11.3.3 Catalysts

Catalysts (industrial and automotive) include Pt, Rh, Pd, Ce, Ni, La often coated onto an alumina-based ceramic support or a metal monolith substrate. The recovery of precious metals depends on their accurate determination in the ceramic material at levels ranging from ppb upwards. Microwave-assisted digestion is recommended to keep the sample preparation time within reasonable limits [183]. ICP-MS and XRF have been compared [158].

The automotive catalysts contain an active coating, mainly consisting of metallic Pt on different carrier materials such as a wire mesh or alumina, carbon, or an organic resin. The main analytical problem is the lack of homogeneity of the materials. A sample of 300 g can be required in order to obtain accuracy within 2% in chemical methods of analysis. In practice 10–15 g portions are used. The dissolution of catalysts is often difficult and time consuming because of the refractory alumina material. In spent catalysts the used catalytic material often introduces insoluble contaminants. A fire assay may be not able to cope with the high alumina content [181]. The sample is usually leached with *aqua regia* and Pt is coprecipitated with Te. A mixture of H_2O_2 and HCl has yielded good results in leaching Pt deposited on Al_2O_3 (reforming catalysts). The final determination is usually photometric. Direct techniques (GD-MS or XRF) are preferred [107]. Percentage levels in aluminosilicate catalyst of Al, Fe, Ti, V, Ni, Mo, Na and Si after decomposition with $\text{HF-HNO}_3\text{-H}_2\text{SO}_4$ by FAAS [182] have been determined.

11.4 NUCLEAR MATERIALS

These include nuclear fuels and their intermediate products such as U, Pu Th and their compounds, low-neutron cross section engineering materials (Zr, Nb and alloys) and reactor coolants (alkali metals). Trace levels must meet the most stringent quality control specifications.

Impurities in fuel can attenuate nuclear processes, those in clad materials increase irradiation whereas in coolants they are important to monitor the corrosion of tubing. Analysis of nuclear fuels up to 1985 by ICP AES has been exhaustively reviewed [184]. Determination of trace impurities in nuclear fuel components by NAA has been discussed [185]. The role of MS in the analysis of the nuclear materials [94] and in nuclear industry in general [186] has been discussed. Analytical procedures are summarized in Table 11.7.

TABLE 11.7

Multielement trace analysis of nuclear materials

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref.
Uranium, UO_2 , U_3O_8 (2 g)	HNO_3	sorption on Cellulose- Hyphan	ICP AES, FAAS	Be, Bi, Cd, Co, Cu, Eu, Fe, Mn, Ni, Pb, Yb, Zn	187
U compounds (ng)	HNO_3	reversed-phase chromatography on tri(2-ethyl- hexyl)phosphate- Kel F	ICP AES	40 elements	188
U_3O_8	n.g.	none	GF AAS	Ag, Be, Ca, Fe, Pb, Sn	189
U_3O_8	HNO_3 (bomb)	extrn. of U with TOPO (cyclohexane)	ICP MS	Ag, Ba, Cd, Co, Cr, Cu, In, Li, Mn, Ni, Pb, Sr, Ti, V, Al, Pb, Y, REE	190
U_3O_8	n.g.	none	ICP AES, GF AAS	Al, Cu, Mg, Mn	191
U_3O_8 (0.3 g)	HNO_3 (bomb)	TBP extrn.- chromatography	ICP AES	Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb	192
Plutonium (0.3–0.8 g)	HCl , HNO_3	anion exchange	ICP AES	30 elements	193

continued

TABLE 11.7 (*continuation*)

Material (amount)	Dissolution	Separation and/or preconcentration	Detection technique	Elements	Ref.
Thorium oxide		carrier distillation with a mixed carrier, viz. AgCl+SrF ₂	ICP AES	Al, B, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Na, Ni, Pb, Si, Sn, Ta, Ti, Te, V, W, Zn	194
Lithium, LiH (0.5 g)	dil. HNO ₃	none	ICP MS	19 elements	195
Lithium (1 g)	H ₂ O	none	GF AAS	Cr, Ni, Pb	196
Boron (0.5 g)	HNO ₃ (1+1)		ICP MS	Cr, Cu, Fe, La, Mg, Mn, Ta, Ti, W, Zr	195
Niobium (1 g)	HF-HNO ₃	cation exchange	ICP AES	Ag, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni Sr, Ti, Zn	79
Niobium (0.5 g)	HF-HNO ₃	anion exchange	ICP AES	Cr, Fe, Mg, Mn, Mo, Ta, Ti, W	197
Niobium (1 g)	HF-HNO ₃	cation exchange	ICP AES, ICP MS	Bi, Cd, Co, Cu, Fe, Hg, In, Ni, Zn	198
Niobium pentoxide (1 g)	HF-HNO ₃ (bomb)	none	FAAS	Ba, Ca, Fe, K, Mg, Na	199
Zr-alloys (2 g)	HF-HNO ₃	none	ICP AES	Al, B, Cd, Co, Cr, Cu, Fe, Hf, Mg, Mn, Mo, Nb, Ni, Sn, Ta, V, U, W	200
Zr-alloys (0.25 g)	HNO ₃ -HF	none	ICP MS	Cu, Hf, Mn, Ti, U	201
Zr-alloys (0.5 g)	HF-HNO ₃	none	ICP MS	Gd, Sm, Th, U	94
Zr-alloys (5 g)	HCl-HF- HNO ₃	none	FAAS	Cd, Cu, Mn, Ni, Pb	202

Uranium

Direct analysis of uranium oxides by XRF [203] and LA ICP MS has been reported [204]. The complexity of AES spectra for actinides prevents direct analysis. Anion-exchange separation prior to ICP AES has been developed [193]. Interferences from the U matrix in ICP AES have been discussed. Uranium hexafluoride has been analyzed directly [205]. Analysis of oxide (U_3O_8) by ETA AAS without preliminary separation was reported [189]. In ICP MS uranium suppresses the analyte signal and its removal is essential to obtain adequate sensitivity [190]. An extraction technique of the U-TOPO complex has been reported [190]. Separation of metal impurities from uranium by anion exchange [206] or on cellulose collectors has been discussed [187].

Thorium

Thorium is a potential fertile material for the production of ^{233}U fissile isotope [194]. Natural and synthetic thorium oxides are highly resistant toward HCl and must be decomposed in a pressure vessel. Dissolution of ThO_2 in condensed polyphosphoric acids is slow, whereas metallic Th is dissolved on heating. Even ignited ThO_2 is rapidly dissolved on heating with orthophosphoric or diphosphoric acid [4].

Plutonium

Plutonium, its oxide (PuO_2) and mixed Pu(IV)–U(IV)–Th(IV) oxide based fuels are dissolved by heating with H_2SO_4 ($(\text{NH}_4)_2\text{SO}_4$ added) in the presence of HNO_3 . The dissolution is catalyzed by fluoride.

Alkali and alkaline earth metals

These react smoothly with humid air and violently with water, giving a solution of the corresponding hydroxide. The effervescent reaction generates hydrogen and heat which would seem to be the ideal conditions for the formation of the volatile hydrides of As, Se, Ge, Sn, Sb, Te, Pb, and Bi and the formation of mercury vapour. When alkali and alkaline earth metals are dissolved directly in acid, a large pH gradient is formed in the solution and certain elements are likely to precipitate in the alkaline phase which may not necessarily re-dissolve in the acidic phase. Both effects induce considerable losses [195]. The sodium matrix is distilled off under vacuum prior to analysis by FAAS or GF AAS [196].

Boron

Boron is dissolved in 50% HNO_3 . In open systems a residue is formed. Pressure dissolution was found to be successful especially when microwave assisted [207].

Niobium

Niobium is resistant to all acids (including *aqua regia*), except HF because of the presence of protective oxide layer. The best solvent is a mixture of HNO_3 -HF in which at slight warming Nb dissolves with violent formation of fluoride or oxofluoride complexes. Adding water converts fluoride to oxofluoride complexes [198]. The direct analysis of niobium by ICP AES is difficult because of the line-rich spectrum. ICP AES on anion exchange in HCl and HF media has been developed for high purity niobium [197]. Activation analysis has been extensively developed and applied to trace analysis of niobium [73].

Zirconium alloys (zircalloy)

Instrumental NAA is a convenient analytical technique for multielement analysis [208]. For other techniques dissolution with HNO_3 -HF is suitable.

11.5 QUALITY CONTROL AND ASSURANCE

Contamination control

This is crucial and sample preparation under class-100 clean bench conditions is strongly recommended for high purity materials. Removal of surface impurities (by degreasing with an organic solvent and acid etching) is the first step to successful analysis [38,116,118]. Minimum requirements include avoiding fluxes, use of closed vessel decomposition and ultrapure acids prepared by the user. Volatilization procedures generally give lower blanks than solvent extraction for gallium [58]. For selenium cation exchange was preferred to charcoal sorption for the same reason [113,209].

Quality assurance

Checking the yields of combined procedures with radiotracers is highly recommended. CRMs are to a large extent unavailable and must be prepared in house and validated with various techniques, especially gases which are prepared with elemental additions but data on stability of such gas mixtures have not so far generally been available [139]. Russian reference materials for ferrous metallurgy have been discussed [210]. Several CRMs available for trace analysis of industrial samples are summarized in Table 11.8.

TABLE 11.8

Selected certified reference materials for trace industrial analysis

Material	Description	Certified trace (<100 ppm) elements
NIST SRMS 665, 1265	electrolytic iron	B, Co, Cr, Cu, Mn, Mo, Pb, Si, Ti, V
NIST SRMs 361–364	low alloy steels	Ag, Au, B, Ca, Ce, Ge, La, Mg, Nd, Pb, Sb, Sn, Te, Zn, Zr
NIST SRMs 2165–2167	low alloy steels	Ag, Al, As, Co, Mo, Nb, Pb, Sb, Sn, Ti, V
NIST SRMs 1765–1767	low alloy steels	Ag, Al, As, Co, Cr, Cu, Ni, Mo, Pb, Sn, Ti, V
NIST SRMs 661,663	low alloy steels	Ag, Au, B, Bi, Ce, Ge, La, Pb, Nd, Sb, Te, Zn
BCR CRMs 074, 075	high purity copper	Ag, As, Bi, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sb, Se, Sn, Te, Zn
NIST SRMs 393–40	high purity copper	Ag, Al, As, Au, Bi, Cd, Cr, Co, Fe, Mg, Mn, Ni, Pb, Se, Sb, Sn, Te, Zn
BCR CRMs 286–288	high purity lead	Ag, As, Bi, Cd, Cu, Ni, Sb, Se, Sn, Te, Ti, Zn
NIST SRM 685	high purity gold	Ag, Cu, Fe, In
NIST SRMs 680, 681	high purity platinum	Ag, Au, Cu, Fe, Ir, Mg, Ni, Pb, Pd, Rh, Zr
BCR CRMs 321–327	unalloyed zinc	Al, Cd, Cu, Fe, In, Pb, Sn, Tl
NIST SRMs 682,683,728	unalloyed zinc	Ag, Cd, Cu, Fe, Pb
BCR CRMs 351–355	Zn–Al alloy	Cd, Cu, In, Mg, Ni, Pb, Sn, Tl
BCR CRMs 356–361	Zn–Al–Cu alloy	Cd, Fe, In, Mg, Ni, Pb, Sn, Tl
NIST SRM 858	Al alloy	Cr, Ni, V
NIST SRMs 897–899	Ni–base superalloys	Bi, Pb, Se, Te, Tl
NIST SRMs 625–631	Zn–base alloys	Cd, Cr, Mn, Ni, Pb, Sn

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Organic industrial materials

This group of materials includes fossil fuels (crude petroleum, oil shale, tar sands, coal and peat) and products of their distillation (hydrocarbons used as solvents or synthetic fuels), or chemical processing (lubricating oils and polymers). From the analytical point of view organic industrial materials are divided into fairly homogeneous liquids (petroleum and its refinery products), solid fuels (coal, oil shale, peat, tar sands) and polymers.

PETROLEUM AND PETROLEUM PRODUCTS

Crude oils and various refinery streams are analyzed for elements (especially Ni and V) which are harmful for catalysts used in oil refinery processes [1]. *Organic solvents* are pure distillation fractions of crude oils or products of organic synthesis. Their trace analysis is essential whenever they are used as extraction solvents, liquid chromatography mobile phases, diluents for viscous oils or solvents for polymers. *Fuels*, usually petrol, are generally analyzed for organometallic compounds added to improve their properties (organolead and manganese compounds). *Lubricating oils* are analyzed for wear metals (Fe, Cu, Ni, Sn, Pb, Cr, Al, Mo) to monitor engine wear patterns, contaminant elements (Si, B, Na) to account for dirt intrusion and leaks, and additive elements (Ba, Zn, P, Ca) [2].

Sample handling prior to measurement

Dilution

The viscosity of many oils is too high to allow their conventional nebulization. The use of preheated sample [3] or high pressure [4]

nebulizers or sample dilution is required. Xylene is a satisfactory diluent for most of the samples. Tetrahydrofuran (5%) can be added to enhance solubility. Hexane and benzene give smoky, unstable flames and plasmas, and therefore should be avoided. Viscosity is controlled by maintaining the oil content of the final sample between 5 and 20%. Direct dilution is applicable to gasolines, light oils, pourable and sticky, crudes and fractions, asphalts, resins and lubricating oils. Dilution may be carried out manually or in an automated system [5–7]. Solvent mixtures in which both oil samples and ionic element standards are soluble have been reviewed [8].

Emulsions

Emulsogenic reagents, e.g. Emulsogen M, NSG surfactant or di-propylglycol enable dilution with water but organometallic standards need to be used [8]. Formation of oil-in-water microemulsions was proposed to simplify the introduction into the ICP [9].

Dry ashing

Dry ashing involves driving off low boiling components at 150–200°C using an IR heater, followed by ignition at 500–550°C in a muffle furnace and dissolution of the ash in a HNO_3 –HCl mixture [10]. Volatile elements (Zn, Cd, Pb) but also others, if present in volatile organic complexes (Ni and V porphyrins), may be lost. Alternatively, the sample is treated with H_2SO_4 prior to ashing in a muffle furnace to char the organic matter and thus to minimize the volatility of the analyte species [11]. Barium and Pb may be lost in the residue whereas As, B, Hg and Se volatilized. Recoveries are improved by ashing in a low temperature oxygen plasma [12,13]. Mercury and Se are lost in any case whereas Ti, Fe, Al and possibly V, Cu, Mo, U are partially volatilized in the presence of more than 100 ppm of halogens [12].

Wet digestion

Wet digestion with HNO_3 has the benefit of retention of volatile elements which might be lost on dry ashing but it generally fails in open systems at 200°C [12] and for some samples even at higher temperatures in pressure bombs. Microwave-assisted digestion may be of advantage.

Dilution vs ashing

Dilution is valid provided that the analyte is present as a soluble complex. Oils often contain suspended and colloidal inorganic materials,

e.g. metallic particles in lubricating oils. Dilution may not retain the sample homogeneity if larger particles are present and then wet digestion and ashing procedures should be considered. Samples rich in suspended matter and two-phase oil–water mixtures always require decomposition. The advantage of the latter is that the matrix is converted from an organic to a dilute mineral acid medium, thus alleviating standardization problems. Ashing is therefore recommended for reference measurements.

Extraction

Extraction (usually with DMF) is sometimes applied to separate the porphyrinic (extract) and non-porphyrinic (residue) fractions of V and Ni contents [14,15].

12.1.2 Determination techniques

Flame AAS and ICP AES are the most popular techniques but ICP MS and TXRF are more competitive and enjoy increasing popularity. Spectrophotometry is inappropriate as it is a monoelement technique and requires time-consuming sample pretreatment, XRF and INAA are suitable but require a large capital investment. Analysis of crude oils and by-products has been reviewed [15,16] with particular emphasis on AAS [8,10,12], plasma spectrometry [11,17] and lubricating oils [8]. Analytical methods for the analysis of petroleum and petroleum products are summarized in Table 12.1.

Atomic absorption spectrometry

Flame AAS is preferred [8,10,12]. An internal standard is required to compensate for different matrix viscosities if only one set calibration standards is to be used. Cobalt was found satisfactory [2,5,24]. Behaviour of various organic solvents and analytes in GF AAS were discussed [25]. A high charring temperature is necessary to reduce the non-specific absorbance. Tungsten coated tubes are beneficial [25].

Inductively coupled plasma atomic emission spectrometry

The success is dependent on operating a stable plasma when an organic solvent is nebulized [26]. High power Ar–N₂ plasmas (4 kW) are advantageous for organic solutions over low power (<2.5 kW) plasmas. Operating conditions are more critical than in the case of aqueous solutions. The organic vapour load can be controlled by adjusting the

TABLE 12.1

Multielement trace analysis of petroleum and petroleum products

Sample	Preparation	Elements determined	Detection technique	Ref.
Crude oil	oil-in-water microemulsion	Al, Mg, Cr, Fe, Ni, Cu, Mo, Ag, Sn, Pb, Ti	ICP MS	9
Heavy crude oils distillates	extraction with DMF	Cu, Fe, Na, Ni, V	FAAS	15
Oil	dilution with CHCl ₃	Cr, Cu, Fe, Mn, Pb, Ti, V, Zn	TXRF	18
Lubricating oils	7.5-fold dilution with xylene	Ag, Al, Ca, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti, V, Zn	FAAS, ICP AES	2
Lubricating oils	dilution with xylene	Ag, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V	ICP AES	6
Lubricating oils	10-fold dilution with xylene	Ag, Al, Ba, Ca, Cr, Cu, Fe, Mg, Mo, Na, Pb, P, Si, Sn, Zn	ICP AES	7
Lubricating oils	5-fold dilution with tetraline	Ag, Al, B, Ba, Ca, Cd, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, V, Zn	ICP AES	19
Fresh and spent lubricating oils	none	Al, Ba, Br, Ca, Cr, Cu, Fe, Mo, Pb, Si, Sn, Zn	WD XRF	20
Oils and greases	10-fold dilution with toluene	Al, As, Ba, Ca, Co, Cr, Cu, Fe, Ga, K, Mn, Ni, Pb, Se, Ti, V, Zn	TXRF	13
Oils and greases	plasma ashing	Al, As, Ba, Ca, Co, Cr, Cu, Fe, Ga, K, Mn, Ni, Pb, Sr, Ti, V, Zn	TXRF	13
Fuel oil	10-fold dilution with white spirit	As, Be, Cd, Cr, Co, Fe, Mn, Mo, Na, Ni, Pb, REE, V, Zn	ICP MS	21
Fuel oil	10-fold dilution with xylene	As, Be, Ca, Cd, Co, Cr, Fe, Na, Ni, Mn, Mo, Pb, V, Zn	ICP MS	22
Glycol based fluids	20-fold dilution with water	Al, Ca, Cu, Fe, Mg, Pb, Sn, Zn	ICP AES	23

aerosol introduction rate to the nature of the solvent [27,28] or by aerosol cooling (thermostatted spray chambers) [14,29]. Xylene is the solvent of choice but the use of tetraline has been reported to minimize the matrix suppression [19]. A V-groove nebulizer which enables particles up to 10 μm in size to be transported is recommended [5,30]. Spectral interferences may be due to Ca (which is present up to 3.5%) which interferes with the Si 251.6 nm and Fe 238.2 nm lines [5]. Background may vary with different samples. In general, ICP AES offers superior freedom from matrix interferences, greater linear range and better detection limits than FAAS, particularly for B [14]. It is the method of choice for lighter elements (Li, Mg, Ni, V) but suffers from insufficient sensitivity for Pb.

Inductively coupled plasma mass spectrometry

ICP mass spectrometry offers detection limits of 10–50 ng g^{-1} which are by a factor of 10–100 lower than those obtained for ICP AES. Virtually no interferences are observed for elements with masses above 80 daltons whereas lighter elements, especially ^{24}Mg , ^{25}Mg , ^{26}Mg , ^{44}Ca , ^{45}Sc , ^{46}Ti and ^{46}Ca are interfered with polyatomic ions. The major difficulty in MS is that the interface is intimately immersed onto the plasma from an end-on position [22]. The Ar plasma does not combust the organics in spite of the high temperatures. The resulting carbon atoms recombine on cool surfaces of the sampling interface and the MS lens. A small amount of oxygen must be added. The CO_2 formed is removed by the vacuum system. The temperature fluctuation in the spray chamber can be observed as small temperature changes can change drastically the solvent loading. Cooled thermostatted spray chambers (below 0°C) [31] or water-jacketted double-pass spray chambers have been used [21].

Instrumental neutron activation analysis

Vanadium, Cr and Sb are determined by short-term activation; the ^{38}Cl ($t_{1/2} = 38$ min) and ^{52}V ($t_{1/2} = 3.9$ min) can be resolved from the decay curve [32–35]. Radiochemical removal of the ^{24}Na continuum was employed in determining Fe, Ni, Co, Zn, Mo and Au in crude oil, distillation fractions, asphalts and related materials [36].

X-Ray fluorescence

Both WD XRF and ED XRF can be applied to direct analysis but need cumbersome standardization and data evaluation [37–39]. The limits of

detection (*ca* 100 ppm) are also sometimes not adequate [20]. Matrix effects may be minimized by the removal of the organic matrix by oxidation or virtually eliminated by preparing specimens as thin films. TXRF eliminates these drawbacks. Direct preparation from dilute solutions of oils yields good results down to $1\ \mu\text{g g}^{-1}$ [13,18]. TXRF followed by low temperature oxygen plasma ashing leads to detection limits down to ng g^{-1} [13].

12.2 ENERGY-RELATED SOLID MATERIALS

This group includes coal, peat, oil shale and tar sands. The need for their analysis arises from ecological (pollution by As, Se, Be, Pb, Tl, Sb), industrial (fouling of hydroconversion catalysts by Ni, As, V, Fe porphyrins) and biogeochemical prospecting concerns [40].

12.2.1 Sample handling prior to measurement

Total recovery of the elements requires the destruction of the organic matter and the dissolution of the siliceous material.

Dry ashing

Dry ashing can be performed at *ca* 425°C to combust the organic matter only or at 750–850°C to convert the carbonate material to oxide. Losses of As, Hg and Se occur whereas other elements can be occasionally lost [41]. Higher recoveries, especially of As and Se, were reported with LTA (at *ca* 100°C) which is time consuming [42]. Dry ashing followed by HF treatment was found to be the most satisfactory procedure for peat [43].

Wet mineralization

Wet mineralization in a pressure bomb with a mixture of HNO_3 – HClO_4 [44] *aqua regia*–HF [42] or HNO_3 – HClO_4 –HF [43,45,46] has been widely used. Microwave assisted digestion is a time-effective approach [44,46,47]. Conventional and microwave digestion procedures were compared [44].

Separation and preconcentration

These are seldom used as the coal matrix is fairly simple and dry ashing offers already a 10-fold preconcentration. During wet ashing

TABLE 12.2

Multielement trace analysis of coal and peat

Sample	Preparation	Elements determined	Detection technique	Ref.
Peat	dry ashing	Al, Ca, Cu, Fe, K, Li, Na, Mg, Mn, Zn	FAAS	43
Peat	digestion with HNO ₃ -HClO ₄ -HF	Al, Ca, Cu, Fe, K, Li, Na, Mg, Mn, Zn	FAAS	43
Peat	digestion with HNO ₃ -HClO ₄ -HF	Al, Ca, Cu, Fe, K, Li, Na, Mg, Mn, Zn	FAAS	46
Coal	10% slurry in 1% Triton	Cu, Fe, Mn, Ni, V	ICP AES	50
Coal	microwave assisted digestion with HNO ₃ -HClO ₄	Fe, Ni, V	GF AAS	44
Coal	slurry	68 elements	ICP MS	52
Coal	slurry	Al, Ca, Fe, Si, Mg, Mn, Ti	ICP AES	51

dilution occurs and the detection limits may not longer be met with enrichment being required, e.g. by using poly(dithiocarbamate) resin [45].

Slurries

Slurries (10–25%) of particles smaller than 30 μm , stabilized with 1% Triton, are favoured because of minimum sample pretreatment and compatibility with GF AAS [47,48], ICP AES [49–51] and ICP MS [52]. Slurry of whole coal with Ni(NO₃)₂ (matrix modifier), Mg(NO₃)₂ (ashing aid), HNO₃ and ethanol (wetting agent) can be introduced into the graphite furnace of AAS [53].

12.2.2 Determination techniques

Analytical methods used for fossil fuels are summarized in Table 12.2. Multielement techniques are generally preferred.

Flame AAS [43,46] has widely been used despite its monoelement character because of the simplicity and cost effectiveness. Electrother-

mal AAS [44,48], also with STPF [48] was used occasionally for the determination of particular elements, e.g. As and Pb [48]. *ICP techniques* for fossil fuels have been reviewed [41]. ICP AES has been widely used in combination with slurry sampling [49–51]. Semiquantitative ICP MS analysis using calibration with a single internal standard (Rh) was developed [53]. *Wavelength dispersive XRF* is capable of direct multielement analysis of coal powders [54] but suffers from calibration problems owing to the lack of standards. Synthetic calibrants are difficult to produce because of the great variation in speciation of the elements found in coal. Thin films should be used to alleviate matrix effects. *Instrumental neutron activation analysis* is favoured for multielement analysis of coals as the matrix does not generally produce long-lived γ -emitting isotopes [55]. Sample weight must be kept low to reduce the activity induced in elements such as Na, Co and Sc. High Al content makes short irradiation INAA difficult.

12.3 POLYMERS

Polymers, synthetic fibres and fabrics are analyzed for residues of catalysts, stabilizers, fillers, pigments and lubricants.

Sample handling prior to measurement

Certain polymers are dissolved in an organic solvent, preferably MIBK, which may be aspirated into the flame. The usual approach, however, is wet digestion with a mixture of concentrated H_2SO_4 and H_2O_2 [56] which is not always satisfactory. When alkaline earths or lead are present the sulphates formed can be dissolved by EDTA in $\text{NH}_3(\text{aq})$ [57,58]. Carbon black [59] can be eliminated with fuming HNO_3 . Silica may precipitate so NH_3 -EDTA medium is recommended to avoid adsorption of traces [56]. The procedures using H_2SO_4 - H_2O_2 - NH_3 -EDTA and H_2SO_4 - H_2O_2 - HNO_3 have been compared [60]. Perlon and nylon were digested at 300°C in an H_2SO_4 - HNO_3 mixture [61].

Determination techniques

A series of papers on the analysis of PVC by FAAS has appeared [46,48,56–61]. Direct insertion of plastics into GF AAS is convenient to match the low levels encountered and to overcome the need for often cumbersome dissolution [61]. The background is high and Zeeman background correction is recommended. Mass spectrometry upon laser

ablation and ICP excitation was applied to polypropylene, polyester, PVC, nylon and PE. ^{13}C was used as an internal standard for semiquantitative analysis [62]. Standards are required for quantitative studies. Instrumental NAA is favoured since the typical polymer (polyethylene, polyurethane and polymethylmethacrylate) matrix (C, O and H) does not activate significantly upon irradiation. Activation analysis does not require digestion and so allows to avoid losses of trace elements and contamination to be avoided [63–65]. Some problems occur with polymethylmethacrylate samples as the evolution of gas resulting from radiation damage is possible. Short irradiation times are used. X-ray fluorescence gives detection limits of 1–100 ppm. Energy-dispersive XRF has been discussed for the analysis of nylons and PVC [66].

12.4 SPECIATION ANALYSIS OF FOSSIL FUELS

Porphyrin complexes of some metals (Ni, V, Fe) are typically distributed over fractions with a large molecular weight range and speciation information is essential for their effective removal. Capillary GC seems to be fairly well suited to the separation of metalloporphyrins. They show remarkable thermal stability but low volatility so that high temperature Al-clad columns are usually required [67–71]. Vanadium and nickel porphyrins in crude oils have also been separated by size exclusion [72–76] and reversed-phase chromatography [72]. Molecular characterization of non-porphyrin trace metal compounds of geochemical and process significance using LC with element-selective detection has been discussed [76,77]. Reversed phase LC of metalloporphyrins has been studied [1,78]. Methods for the speciation analysis of metalloporphyrins are summarized in Table 12.3.

12.5 QUALITY ASSURANCE

Calibration

Aqueous standards are suitable only if the matrix is destroyed prior to analysis. Generally organometallic calibration standards dissolved in the solvent used for the sample dilution should be used. The preparation of calibration solutions from solid organometallic compounds has been discussed [10].

TABLE 12.3

Species selective analysis of fossil fuels

Sample	Species determined	Separation	Detection technique	Ref.
Oil shale	Ni- and V-porphyrines	open-tubular GC	MS	68
Crude oil, gasoline	Ni- and V-porphyrines	open-tubular GC	MIP AES	70
Heavy crude oils, asphaltenes	Ni- and V-porphyrines and non-porphyrine complexes	reverse-phase HPLC	GF AAS	73
Crude oils, asphaltenes	Ni- and V-porphyrines and non-porphyrine complexes	size-exclusion chromatography	GF AAS	72, 73
Oil	Ni- and V-porphyrines and non-porphyrine complexes	size-exclusion chromatography	ICP AES	74
Heavy crude oil	V- and Ni-complexes	size-exclusion chromatography	ICP AES	76
Petroleum crudes and residues	V-complexes	size-exclusion chromatography	ICP AES	75

Contamination

Contamination during sampling cannot be neglected. Exposure to metallic surfaces should be avoided. Solder seams in metal containers often used for sampling can give rise to significant contamination. Some polymers may contain significant levels of catalyst residue remaining from their manufacture. Plastic bottles may exhibit porosity to certain solvents and glass vessels may be preferred. Checks should be made for blanks and carry-over contamination. In many industrial environments the presence of dust and fumes may cause problems. Clean or filtered air facilities are required for work with electrothermal AAS where the

amount of sample is small. Sodium and Zn are commonly found in organic solvents so redistillation or extraction with mineral acids is often necessary to purify reagents further. Ashing or wet oxidation methods require pure acids. Blank levels should be monitored in all cases.

Losses

Losses are common during dry ashing and evaporation procedures as some elements may be present in volatile organometallic forms.

Validation

Certified reference materials available for coals and oily matrices are summarized in Table 12.4.

TABLE 12.4

Selected certified reference materials for trace analysis of organic industrial materials

Material	Elements certified
SARM 18 Witbank Coal	Ba, Be, Ce, Co, Cr, Cu, Fe, Hf, La, Mg, Mn, Ni, Rb, Sc, Sm, Sr, Th, Ti, V, U, Zr, Zn
SARM 19 OPS Coal	As, Ba, Be, Ce, Co, Cr, Cu, Fe, Ga, Hf, Hg, La, Mg, Mn, Na, Ni, Pb, Rb, Sc, Se, Sm, Sr, Th, Ti, Tl, V, U, Y, Zr, Zn
SARM 20 Sasolburg Coal	As, Ba, Be, Ce, Co, Cu, Fe, Ga, Hf, Hg, La, Mg, Mn, Na, Ni, Pb, Rb, Sc, Se, Sm, Sr, Th, Ti, Tl, V, U, Y, Zr, Zn
NIST SRM 1632a Coal	As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sc, Se, Th, V, U, Zn
NIST SRM 1632b Coal (bituminous)	Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, Se, Th, Ti, U, Zn
NIST SRM 1085a Lube Oil	Ag, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Sn, Ti, V
NIST SRM 1634b Fuel Oil	As, Fe, Mn, Ni, Se, V, Zn
NIST SRM 1635 Coal (subbituminous)	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Th, U, V, Zn
BCR CRM 040 Blend Coal	As, Cd, Co, Cr, Hg, Mn, Ni, Pb, Zn
BCR CRM 180 Gas Coal	As, Cd, Hg, Mn, Pb, Se, V, Zn
BCR CRM 181 Coking Coal	As, Cd, Hg, Pb, Se, V, Zn
BCR CRM 182 Steam Coal	Cd, Hg, Mn, Se, V, Zn

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Aluminium

Aluminium (Al, atomic weight 27.0, melting point 660°C , $d = 2.79 \text{ g cm}^{-3}$) is a moderately hard, grey metal. It is the third most abundant element, constituting 8.13% of the earth's crust, but it is a trace element in the biosphere owing to the low solubility of its ores in natural waters [1–3]. Aluminium plays an important role in pathogenesis of clinical disorders and, in particular, must be monitored in serum of dialyzed patients and in dialysis fluids [2]. In the environment erosion of Al from soils and rocks by acid rain contributes to the pollution of surface waters [1–3].

Aluminium is resistant to HNO_3 owing to the protecting oxide coating but it dissolves readily in *aqua regia* and, unless very pure, in dilute mineral acids and with liberation of H_2 . The metal dissolves in hot alkalis with formation of $\text{Al}(\text{OH})_4^-$. Aluminium occurs in the III oxidation state. The simple ion exists as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ which dissociates producing a series of ions some of which tend to polymerize. The hydroxide, $\text{Al}(\text{OH})_3$, is amphoteric. Aluminium forms stable complexes with fluoride, oxalate, EDTA and tartrate, and weak complexes with acetate.

13.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction is used mainly for the preliminary separation of metals which might interfere in the instrumental determination of Al. Extraction of Al with 8-hydroxyquinoline is sometimes used in combination with spectrophotometry.

Sorption

Cation exchange has been used to separate traces of Al from gram amounts of Tl [4]. The cation-exchange of Al on the Dowex 50W-X2 microcolumn was progressively inhibited by acetate and chloride and was interfered with by Ca and Mg present in the dialysis fluid samples [5]. Anionic complexes of Al with Tiron [6] or Pyrocatechol Violet [7] are retained on anion exchange resins and can be eluted with dilute HCl. Alternatively, anion exchangers can be modified with Chromotrope 2B [8] or CAS [9,10] to retain Al selectively in the presence of Pb, Zn, Ni, Cd, Ca and Mg. Aluminium can be eluted with acids [8] or alkalis [9], often in *on-line* mode. Retention by anion exchange at pH 7 was suitable for water [11] and dialysis fluids [5,11] but failed for serum in which Al is bound strongly by proteins [11]. Anions that form complexes with Al such as EDTA, phosphate and fluoride interfere. Aluminium can be quantitatively retained on cellulose [12] or CPG [13–16] modified with 8-hydroxyquinoline [12–14] or other complexing agents [14,17], and then eluted with dilute acids, often in *on-line* systems [13,15]. Retention of Al on Chelex-100 (pH 5–6) with subsequent elution with 2.5 M NaOH has been reported [5].

Coprecipitation

Coprecipitation of Al with Fe(III) in the presence of 8-hydroxyquinoline has been used [18]. Traces of Al can be precipitated at pH 4.5–5 (acetate buffer) using Ti, La, Zr or Fe(III) as scavenger. Micelle-enhanced ultrafiltration has been proposed [19].

13.2 DETERMINATION TECHNIQUES

Spectrophotometry

The extraction method using 8-hydroxyquinoline is not very sensitive ($\epsilon = 7.3 \times 10^3$ at 390 nm, CHCl_3) but is highly selective provided that appropriate masking agents are added. More sensitive methods ($\epsilon > 10^5$) are based on ternary systems including triphenylmethane reagents (CAS, Eriochrome Cyanine R, Pyrocatechol Violet) and surfactants (CTA, CP) [8,20]. Selectivity needs to be improved by reducing Fe(III) with ascorbic acid, masking Cu with thiosulphate and pre separation of some rarer elements (e.g. Be, V, Zr). The usefulness of the CAS method is practically limited to rapid on-site estimations of labile Al in environmental waters. CAS reacts rapidly with monomeric and small poly-

meric forms of Al(III) but is unreactive toward the non-labile polymeric species, colloidal $\text{Al}(\text{OH})_3$ and colloidal aluminosilicates. Interference from fulvic acid and silicate is negligible [20]. Pyrocatechol Violet was used for the determination of Al in speciation schemes [21,22], also in FI [22] mode and as post-column chromogenic reagent [23]. Masking of iron was necessary [22]

Fluorometry

Various fluorescent reagents including Eriochrome Red B [24], 2-hydroxy-1-carbazole carboxylate [25,26], salicylaldehyde carbohydrazone [27] salicylidene-*o*-aminophenol [28] and 8-hydroxyquinoline-5-sulphonate [29] have been proposed with DLs down to $0.1 \mu\text{g/l}$. The sensitivity can be improved by solid phase fluorometry [28,30]. Transition metals, e.g. Zn, Ni, Co, Cu and Fe(II) usually interfere and must be removed or masked.

Flame atomic absorption spectrometry

The recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame [9,13,31] allows a sensitivity of $ca\ 1 \mu\text{g ml}^{-1}$ to be obtained at the most sensitive 309.3 and 396.2 nm lines. The 309.3 nm is actually a doublet (309.27 nm/309.28 nm). Ionization should be controlled by the addition of 0.1% or more of KCl or LaCl_3 . The Al signal is enhanced in the presence of Fe, Ti, BF_4^- and acetic acid. Atomization of Al in the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame is supported by amines [32].

Graphite furnace atomic absorption spectrometry

This offers a characteristic mass of 10 pg using a pyrocoated tube and platform atomization. The most sensitive 309.3 nm line is usually used but in few cases the measurements were made at the 396.2 nm line to improve linearity [33–36]. Background correction is recommended; D_2 [37–44] or Zeeman effect [34, 45–54] were employed with equal frequency. The most common interference is loss of Al as volatile halides [55]. Without the addition of a modifier a pyrolysis temperature of 1400°C is allowed [56]. Pre-atomization losses of Al determined by wall atomization GF AAS have been discussed [57]. The most common modifier is $\text{Mg}(\text{NO}_3)_2$ [47,50,54,58,59] which converts Al into a single thermally stable form, swamps matrix effects and acts as an ashing aid [36]. Addition of $\text{K}_2\text{Cr}_2\text{O}_7$ was found to reduce the formation of gaseous AlO and Al_2C_2 [37,47]. Fluorides were investigated as matrix modifiers [60] but volatilization losses due to the formation of volatile AlF_3 are likely [55]. Sulphate suppresses the Al signal [61]. The effect of phos-

phorus is subject to controversy. Whereas some authors observed signal enhancement due to micromolar addition of H_3PO_4 [61], others observed no effect [62] or even a serious interference by this acid [63]. Some complexing agents and surfactants have been reported to enhance the Al signal by a factor of up to 10 [64]. Suppression of the Al signal by Si was eliminated by the use of platform and pyrolytically coated graphite tube [54]. Reduction of the cycle time by omission of the ashing stage [65] or use of the STPF concept [66] was discussed. Semi-on-line FI GF AAS [40] and solid sampling techniques have been reported [67,68].

Inductively couple plasma atomic emission spectrometry

ICP AES offers DLs down to $10 \mu\text{g l}^{-1}$ at the most sensitive 396.15, 309.27 and 308.22 nm lines. The 309.27 and 308.22 nm lines should not be used for Al concentrations below $1 \mu\text{g ml}^{-1}$ since several OH bands are present around these wavelengths. Only V ($>10 \mu\text{g ml}^{-1}$) interferes at the 308.22 nm line [69]. Calcium and Na are the most serious interferences at 396.15 nm and cause an elevated and sloping baseline. Calcium interference was easily eliminated by background correction [62,70] and the Na content was matched in the standards [62]. Electrothermal vaporization ICP AES offers an ADL in the low picogram range [67,71–73]. Background emission from Ca is removed after addition of H_2 to the purge gas [73]. Variations in emission intensity are overcome by addition of Cs as matrix modifier and using Ga as internal standard [72]. Polytetrafluoroethylene was reported to improve volatilization of Al [74].

Other techniques

Aluminium has only one stable isotope ^{27}Al . The ICP MS signal is interfered with by $^{12}\text{C}^{15}\text{N}$ and $^{13}\text{C}^{14}\text{N}$ [75]. X-ray fluorescence lacks sensitivity. Neutron activation analysis is complex and subject to interferences. Aluminium in drinking water has been measured by NAA (^{28}Al ($t_{1/2} = 2.25 \text{ min}$)) at 1778 keV with a DL of 100 ng Al for a 10-ml sample [76].

13.3 ANALYSIS OF REAL SAMPLES

Aluminium concentrations in geochemical samples (rocks, ores and sediments) are at the percent level and are accessible by a variety of techniques [77]. Aluminium is generally determined as the total element but speciation is of increasing concern. The bioavailable Al which

is of concern in soils can be leached with acetic acid and ammonium acetate solution (pH 7) [18]. Aluminium is often determined in various organic and inorganic industrial materials (*cf.* Chapters 11 and 12) in a multielement array.

13.3.1 General considerations

Contamination

Aluminium is ubiquitous in the environment so the hazard of uncontrolled extraneous additions of Al is serious. Clean room class 100 facilities and carefully evaluated laboratory-ware washing protocols are essential for accurate analysis and have been discussed in detail [49, 68]. Glassware which is the source of contamination even after careful washing [37,67] should be avoided in favour of quartz and polyethylene. Cleaning of quartzware in high purity HNO_3 vapours [78] or by soaking in HNO_3 (1+1) followed by washing with copious amounts of deionized, distilled water [37,77] and eventually with an EDTA solution [37,68] have been recommended. The results of contamination studies in the solid sampling GF AES of biological samples have been presented [67]. A new cup for solid sampling has been designed to reduce contamination during insertion into the tube [68].

Storage and stability

Influence of storage conditions (temperature, vessel type and sample pretreatment) on Al concentrations in serum, dialysis fluid, urine and tap water was studied [79]. Sample storage in glass vessels was unsuitable whereas only minor alterations of Al levels were observed on storage in polypropylene or polystyrene tubes [79]. Loss of Al may be due to adsorption or slow transformation of Al ions into less soluble compounds. Acid washing of glass containers resulted in greater Al adsorption compared with untreated vessels [79]. Acidification of urine was advised since Al might be lost as insoluble phosphate [78,79]. Acidification is advisable for storage of dialysis fluids [79]. If aqueous standards are used for calibration, the pH should be either near 3 or above 8 to ensure that all the aluminium is present in solution [36].

13.3.2 Water, dialysis fluids and pharmaceutical samples

Tap and environmental waters may contain various Al complexes such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^-$ with different solubilities and

ion charge. At $\text{pH} < 5$ soluble Al^{3+} , at $\text{pH} > 7$ AlO_2^- and in neutral solution practically insoluble $\text{Al}(\text{OH})_3$ are present. Additionally Al may be bound to organic and inorganic ligands as well as to the particulate matter. Acidification of tap water samples (to $\text{pH} < 1.5$) is necessary to keep Al in solution [79]. Tap water can be analyzed directly by GF AAS using platform atomization by reference to a pure water calibration graph [62,80]. For other techniques preconcentration, usually by anion exchange (*cf.* Table 13.1) is required.

TABLE 13.1

Methods for the determination of aluminium in waters and dialysis fluids

Sample (amount)	Sample preparation	Detection technique	DL ($\mu\text{g}/\text{ml}$)	Ref.
Waste water	extrn. with HDEHP (molten C_{17} – C_{20} fatty acids)	XRF	0.5	81
Tap water, dialysis fluid	FI anion exchange, elution with 1 M NaOH	ICP AES	0.02	11
Dialysis fluids (spiked)	FI anion exchange, elution with 1 M NaOH or FI Chelex-100, elution with 2.5 M NaOH	ICP AES	0.003	5
Subsurface sea, river water (250–500 ml)	sorption on immobilized 8-hydroxyquinoline resin, elution with HCl – HNO_3	GF AAS	0.08 ^a	16
River and seawater	sorption on 8-hydroxyquinoline on CPG*, elution with HCl – HNO_3	FAAS	0.003	13 15
River water, dialysis fluid	anion exchange of the Tiron complex, pH 6.5, elution with 0.1 M HCl	DCP AES	n.g.	6
Tap water	sorption on Chromotrope 2B loaded anion-exchanger, pH 6, elution with 0.01 M HCl	VIS	n.g.	8
Drinking water	anion exchange of Al–Pyrocatechol Violet complex, pH 7, elution with 0.1 M HCl	DCP AES	n.g.	7

^a pg/ml .

*CPG: controlled pore glass.

Dialysis fluids are composed of Na, K, Ca and Mg chlorides together with either acetate or lactate and glucose at variable proportions. Control of the water supply is the most important parameter in limiting the Al content of the fluid but it is also necessary to monitor Al levels in the raw materials. The concentrates are not easily analyzed since their Al contents is in the very low mg/l range and the overall salt content is very high (ca. 30%). The approaches for direct GF AAS include either considerable dilution of the concentrate and calibration with aqueous standards or small dilution (up to 1+3) and matrix modification [62]. Nitric acid has been proposed as matrix modifier using either an uncoated [82] or a pyrolytically coated tube and platform atomization [33] but high blanks and short graphite tube lifetime occurred. Other modifiers (used with pyrolytically coated tube and platform) included NH_4NO_3 [52] and H_3PO_4 [41]. Dialysis fluids can be analyzed after anion exchange preconcentration by ICP AES [5,11] or DCP AES [6] (*cf.* Table 13.1). Aluminium in calcium gluconate was analyzed by ICP AES after sorption on oxine–cellulose resin [12]. Aluminium in pharmaceutical preparations can be determined by GF AAS directly or on dissolution in HNO_3 , with $\text{Mg}(\text{NO}_3)_2$ as matrix modifier. Detection limits of 40 ng g⁻¹ or 1 ng ml⁻¹ on a solid or liquid basis, respectively, are typical [77].

13.3.3 Biological samples

Graphite furnace AAS is virtually the only technique used. The need for internal quality control samples and suitable reference materials is emphasized [83].

Serum

Serum is analyzed directly by GF AAS (on dilution 1+1 [37,39,47, 50,59,62,80] or larger [45,50,53,78]), usually with a L'vov platform and the STPF protocol. The precision deteriorates when undiluted serum samples are directly injected into the furnace [62]. The diluents include water [62,78], Triton-100 [39,45,46,80,84], sometimes HNO_3 [50,53] or a $\text{Mg}(\text{NO}_3)_2$ solution [39,47,50,59]. Addition of Mg increases the risk of external contamination [62]. A comprehensive optimization study of GF AAS for Al in serum has been presented [36]. Ashing temperatures of 1500–1600°C with preliminary treatment at 500–600°C in the presence of O_2 are used [47]. Background correction with either a D_2 arc [37,39] or the Zeeman effect [45,46,50,53] is frequently used, even if the non-specific absorption of the residual matrix components is rather limited

at these temperatures. Detection limits below 1 ng ml^{-1} are typical at the 309.3 nm line. The method of standard additions is strongly recommended [53]. Inductively coupled plasma AES is suitable for serum samples with Al contents above 30 ng ml^{-1} [62]. The sensitivity of GF AES compares favourably with that of GF AAS [67] and the technique can be used for the direct analysis of blood, serum and dialysis fluid offering DLs down to the low ng ml^{-1} level [71,72]. None of the serum components at normal level interfered with the Al measurements at 309.27 nm [62]. Ultimate quality control is missing in all publications owing to the lack of a serum CRM for the normal Al content. Developments in methodologies have been reviewed [59,85]. Eighty percent of Al in serum is bound to protein and care must be taken to avoid precipitating protein prior to the delivery of the sample into the furnace [36]. The direct calibration method with matrix modification was found to be comparable with acid protein precipitation [86].

Urine

Urine samples are analyzed similarly to serum [34,46,62,78]. Preconcentration of Al by sorption on a poly(acrylamidoxime) resin has been reported [71].

Soft tissues

Soft tissues should be excised with a stainless steel knife and Teflon-coated dissection tools, placed into EDTA-soaked plastic vials and frozen immediately at -70°C [45]. Brain tissues which are very rich in phosphorus and alkali and alkaline earth metals show molecular absorption problems [87]. Samples are usually digested with HNO_3 [48,49,66,73,78,87,88]. Closed-vessel microwave digestion is recommended [49,87]. Fatty residues left after digestion of tissue samples have been reported not to retain significant amounts of Al [48]. The digests are usually analyzed using pyrolytically coated tubes and platform atomization. Either no matrix modifiers [48,49,66] or $\text{K}_2\text{Cr}_2\text{O}_7$ [87], HNO_3 -Triton X-100 [34,88] or $\text{Ca}(\text{NO}_3)_2$ [66] were employed. A fast STPF protocol method with no pyrolysis step and no matrix modifier has been developed [66]. The solid sampling GF AAS with the constant temperature atomizer was reported for the determination of $0.2\text{--}100 \text{ }\mu\text{g g}^{-1}$ in biotissues [67,68].

Hard tissues

Problems with contamination-free homogenization of hard bone tissues (non-metallic homogenizers should be used) have been mentioned

and the brittle fracture technique for sample pulverization has been employed [42]. To minimize sample contamination LTA was preferred to wet extraction [42]. Microwave-assisted digestion with HNO_3 is an alternative [49]. Aluminium in bone digests has been determined using uncoated tubes [78], pyrocoated tubes with L'vov platform and $\text{NH}_4\text{H}_2\text{PO}_4$ matrix modifier [51] or by a fast STPF method with no pyrolysis step and no matrix modifier [66]. Isopropanol was recommended instead of acetone for washing hair samples to avoid contamination [89].

Foodstuffs

The recovery of Al on HNO_3 or $\text{HNO}_3\text{--HClO}_4$ digestion (even if microwave-assisted) was found to be incomplete, especially for food items which could have been in contact with dust or ambient air [70]. A pretreatment with HF is necessary to improve the yield [70]. An alternative is fusion with $\text{Na}_2\text{CO}_3\text{--Na}_3\text{BO}_3$; the large amounts of Na added, however, suppress the absorbance and require matrix matching [43]. Determination of Al in wine [90] and milk [91] has been discussed. The homogeneity of Al at the $\mu\text{g g}^{-1}$ level in agricultural CRMs was checked by GF AAS indicating homogeneous distribution at test portion sizes of 0.25 g [92]. The determination of Al in foodstuffs has been reviewed [93].

13.4 SPECIATION

The most toxic Al species are considered to be $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3$ because of their small size and high diffusion mobility which favour reactions with target proteins [11,77]. This fraction, called "labile monomeric Al", is determined in natural waters as the difference between the total monomeric Al (determined by reaction with Pyrocatechol Violet without prior acidification) and non-labile monomeric Al (determined in the same way but after passing the sample through a cation exchanger) [77]. The monomeric labile Al fraction is determined by cation-exchange chromatography with spectrophotometric [22] or fluorometric [77] detection. Fractionation methods for Al in natural water samples have been compared [94]. A speciation scheme has been developed for the determination of total (after acidification), monomeric (without acidification), non-labile (unacidified after cation exchange) and exchangeable (the difference between monomeric and non-labile) aluminium in fresh-water samples after filtration with various pore sizes [21]. Particulate Al in fresh waters was determined by INAA after filtration, the filtrates were subjected to ion-exchange fractionation in order to separate Al

combined with humic acids, fluoride-complexed Al and free or hydrolyzed Al. The concentrations of Al in different fractions have been determined by ICP AES [95].

Ion-interaction chromatography with fluorometric detection has been used to determine speciation of citrate, tartrate, malonate, fluoro- and oxy-aluminium species (negatively charged, neutral and single, double and triple-positively charged) in soil extracts and plant sap [96]. A method for the identification of fluoro-, oxalato- and citratoaluminium complexes by ion-chromatography followed by derivatization with Tiron and photometric detection has been shown but with no relevance, however, to real samples [97].

Ultrafiltration [98–101] has been used to study protein binding and speciation of Al in blood serum [102]. The possibility of speciation of Al neurotransmitter (noradrenaline, dopamine, adenosine 5'-triphosphate) complexes by SEC-ICP AES has been shown [103]. Size exclusion chromatography with fraction collection GF AAS was also used to study Al binding to albumin, transferrin and other protein in serum [98,99, 104,105]. In the separation of the various forms of Al species in a partially neutralised solution by SEC the perturbation brought about by charge effects has been encountered [106]. Speciation methods are summarized in Table 13.2.

TABLE 13.2

Methods for speciation of aluminium

Sample	Separation method	Column	Eluent	Detection (DL, ng ml ⁻¹)	Ref.
Serum	anion-exchange chrom.	TSK DEAE-5PW	0.05 M Tris-HCl, gradient pH 9.0–9.2	FC GF AAS	107
Serum	anion-exchange chrom.	TSK DEAE-3SW	sodium acetate gradient	FC GF AAS	102
Serum	size-exclusion chrom.	P10, P4		GF AAS	104
Serum	size-exclusion chrom.	Bio-Gel P2	buffer (NaCl, NaOH, KCl, CaCl ₂ , MgCl ₂ , NaHCO ₃ , Tris) pH 7.4	FC GF AAS	98

Sample	Separation method	Column	Eluent	Detection (DL, ng ml ⁻¹)	Ref.
Serum	size-exclusion chrom.	Sephacryl S-300; Sephadex G-50	buffer (NaCl, NaHCO ₃ , HCl, Tris), pH 7.4	FC GF AAS (5)	105
Serum	size-exclusion chrom.	Sephacryl S-300 Superfine	buffer (NaCl, KCl, MgCl ₂ , MgSO ₄ , NaHCO ₃ , NaH ₂ PO ₄) pH 7.4	FC GF AAS (0.3)	99
Freshwater	size-exclusion chrom.	Superose 2HR	0.1 M acetate buffer	VIS	108
Serum	ultrafiltration			FC GF AAS	98–101
Serum	immuno-affinity chrom.	CNBr-activated Sepharose 4B and human transferrin	isotonic phosphate buffer (pH 7.2) with rabbit anti-human transferrin	FC GF AAS (0.3)	99
Freshwaters	filtration and ion-exchange			VIS	21
Lake and tap water	cation-exchange chrom.	Dionex CG2	0.1 M K ₂ SO ₄ , pH 3.0	FLU	77
River, tap water	flow-injection cation-exchange	Amberlite IR-120	none; Al determined in eluate	VIS	22
Natural waters	dialysis or capillary electrophoresis	Amberlite IR-120	none, Al determined in eluate	VIS	94
Soil extracts, plant saps	ion-interaction chrom.	Dionex NS1 (RP18)	gradient elution; I: 1 mM BuSO ₃ H, pH 3–6; II: 1 mM BuSO ₃ H–4 mM NH ₄ Cl, pH 3.0	FLU	96
Standards	ion chrom.	Dionex 2020	0.7 M NH ₄ Cl–HCl; pH 2.0, 3.2, 4.2	VIS	97

FC: Fraction collection.

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Antimony

Antimony (Sb, atomic weight 121.8, melting point 631°C , $d = 6.7 \text{ g cm}^{-3}$) is a silvery white, brittle metal. It occurs in the earth's crust with an average abundance of 0.2–0.3 ppm, principally in stibnite, Sb_2S_3 . The metal dissolves in dilute HNO_3 (with formation of $\text{Sb}_2\text{O}_3(\text{aq})$) and in a mixture of H_2O_2 – CH_3COOH . Antimony occurs in oxidation states –III, III, V; Sb(III) is the most stable. The Sb^{3+} ion does not exist in aqueous solution because of hydrolysis to SbO^+ . Sodium hydroxide precipitates as gelatinous hydroxides from Sb(III) and Sb(V) solutions, soluble in excess of the reagent to form $\text{Sb}(\text{OH})_6^{3-}$ and $\text{Sb}(\text{OH})^-$, respectively. H_2S precipitates orange Sb_2S_3 or Sb_2S_5 from dilute acids. Tin and Fe reduce Sb(III and V) to the metal whereas stronger reductants generate SbH_3 . Sb(III) halides volatilize from boiling strongly acid solutions. Antimony forms halide, sulfate, oxalate and tartrate complexes.

Antimony is a toxic element. The need for the determination of Sb arises mostly from environmental concerns and metabolism studies. Chemical speciation between Sb(III) and Sb(V) and organoantimony compounds: monomethylstibonic acid $\text{CH}_3\text{SbO}(\text{OH})_2$ and dimethylstibonic acid $(\text{CH}_3)_2\text{SbO}(\text{OH})$ is important.

14.1 SEPARATION AND PRECONCENTRATION

Volatilization

Both Sb(III) and Sb(V) react with NaBH_4 to produce the hydride (SbH_3 , stibine). The reaction yield is much poorer for Sb(V) than for Sb(III). Prior to determination of the total element, Sb(V) is usually prereduced to Sb(III) from which the hydride is generated. Any mineral acid (HCl , H_2SO_4 , HClO_4) can be used as medium for the SbH_3 genera-

tion [1]. The reduction is preferably carried out in 1 M HCl in the presence of KI [2–4,5], KI–ascorbic acid [6], or thiourea [2,7]. Antimony(V) can also be reduced electrochemically, in the FI mode [8]. Antimony(III) can be selectively determined in citric acid at pH 2.2 [3,9,10], in 1 M malic or 0.5 M tartaric acid [2] or in H_3PO_4 at pH 1.5–2 [11]. Hydride generation of Sb is interfered by most transition metals, hydride forming elements (Bi, Se) and oxidants. Iron(III) interferes by oxidizing Sb(III) to Sb(V) [12]. Mercury, Cd, Zn do not interfere [13]. The interference from Co, Cu, Ni and Fe(III) can be alleviated by adding thiourea [2,14]. A masking solution consisting of ascorbic acid and thiourea was used to suppress interferences from oxidants ($\text{Cr}_2\text{O}_7^{2-}$, MnO_4^-) and some hydride-forming elements [15]. Sulphide interferes but is usually converted to SO_4^{2-} during oxidative digestion [15]. 1,10-Phenanthroline was used to minimize the Ni interference [16]. Stibine can be generated from Sb(III) in the APDC–MIBK extract [17] or in a slurry in citric acid [10]. Cryogenic preconcentration of SbH_3 is often required to match the low levels of Sb in real samples [3]. Flow injection and CF systems can be used for larger sample throughput [9].

Extraction

Extraction of Sb(V) halide complexes into oxygen-containing solvents from HCl, HBr or HI media is popular [18,19]. Antimony(III) can be extracted as SbBr_3 or SbI_3 from 5 M H_2SO_4 containing bromide or iodide, respectively. Extraction of Sb with dithiocarbamates is a common alternative. The APDC–MIBK system has been studied [17,20–22]. Antimony(III) is extracted over a wide pH range (0–9) whereas Sb(V) is not extracted at pH higher than 2.5 according to some authors, or higher than 5 according to others [23,24]. Tartrate or citrate are added to protect Sb(III) from oxidation or interaction with Sb(V) [21]. Total Sb is extracted after reduction of Sb(V) with KI [25]. Antimony(III) was selectively extracted at pH 9.5 with DDTC into MIBK [22]. Extraction of Sb(III) with bis(trifluoroethyl)dithiocarbamate (and of Sb(V) after reduction with KI– $\text{Na}_2\text{S}_2\text{O}_3$) has been reported [26]. Selective extraction of the Sb(III)–lactate complex as an ion pair with Malachite Green was proposed [27]. Complexes of Sb with lactate [27], mandelate [28] and 2-hydroxy-4-methylpentanoate [29] can be extracted as ion pairs with Malachite Green. The complexes of Sb(III) and Sb(V) differ in terms of stability so the choice of reaction conditions enables differentiation between Sb(III) and Sb(V).

Coprecipitation

Coprecipitation of Sb hydroxide with $\text{La}(\text{OH})_3$ [30,31] or $\text{Fe}_2\text{O}_3(\text{aq})$ collector [18] is popular. Coprecipitation of Sb(III) with thioanilide (total Sb after reduction of Sb(V) with SnCl_2) was reported [32].

14.2 DETERMINATION TECHNIQUES

Spectrophotometry

A large number of methods are based on the extraction of the ion pair of the SbCl_6^- with a basic dye, e.g. Rhodamine B or Crystal Violet ($\epsilon \approx 10^5$). The presence of Sb(V) must be ensured, e.g. by addition of cerium(IV). A DL of $0.1 \mu\text{g ml}^{-1}$ can be obtained but the method shows poor selectivity and requires a prior separation of Sb.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.5 \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 , oxidizing (lean, blue) flame at the most sensitive 217.6 nm line. An EDL is available but the gain in sensitivity is small (10%). High acid concentrations often required to stabilize Sb in solution depress the Sb signal and must be matched in samples and standards. Interference of Fe, Au, Mo and Sn which are co-preconcentrated as chloride complexes during extraction into MIBK can be removed by adding a long-chain quaternary ammonium salt, e.g. Aliquat 336 [33].

Quartz furnace atomic absorption spectrometry

Quartz furnace AAS based on the atomization of SbH_3 offers a detection limit of 0.1 ng ml^{-1} which can be further improved by cryotraping of the stibine [3,4,9,15]. This technique is also used as detector for GC-based speciation studies [34]. Interferences in HG QF AAS of Sb have been discussed [35].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of 0.1 ng ml^{-1} (characteristic mass 20 pg) but is prone to interferences; the problems encountered have been extensively discussed [36]. Iron absorbs at 217.81 nm close to the 217.60 nm Sb line [36]. Overcompensation is severe in Fe, Co and Ni-rich matrices [37]. Antimony is expected to be stable to 900°C in the absence of chloride [38] but in the presence of chloride it is lost from the GF at relatively low pyrolysis temperature. The most common modifiers include HNO_3 [39], $\text{Ni}(\text{NO}_3)_2$ [18,40,41] and a mixture of Pd, Pt, Rh,

Ru and ascorbic acid [42]. The stabilizing effect of the Pd-Mg modifier has been discussed [43]. Five different matrix modifiers (HNO_3 , Cu, Ni, Mo and Pd) have been compared; Pd was found to be the best [39]. The severe FeCl_3 interference was avoided by adding ascorbic acid [44]. Sulphate interferes seriously and its concentration must be matched in calibration solutions [43]. The NiCl_2 interference was removed by the STPF protocol [40]. Platform atomization is preferred to wall atomization in samples containing alkali and alkaline earth metal chlorides (especially MgCl_2 and CaCl_2) despite slightly poorer sensitivity [37]. Experimental sensitivity of GF AAS can be increased by the sequestration of the SbH_3 in a GF [4,6] and also in the FI mode (ADL of 20 pg or DL of 5 ng ml^{-1} was obtained) [6].

Atomic emission spectrometry

Inductively coupled plasma AES offers a DL of *ca* 20–50 ng ml^{-1} at the most sensitive 206.83 and 217.58 nm lines. The interference from Al at 217.58 nm is eliminated by background correction. High Cr concentrations interfere at 206.83 nm. Detection limits are considerably improved down to 0.2–3 ng/ml [2,45] by the introduction of Sb as SbH_3 . A variety of automatic FI or CF systems have been developed, usually for the simultaneous [45–47] or sequential [5] determination of Sb, As and Se (see also Chapters 15 and 49). A direct graphite cup insertion technique has been applied for the determination of Sb in iron and steels [48]. Detection limits of 0.2–1 ng ml^{-1} have been reported for DCP [7].

Mass spectrometry

Antimony has two stable isotopes ^{121}Sb and ^{123}Sb , with relative abundances of 57.25% and 42.75%, respectively [40]. Isotope dilution ICP MS has been reported [30].

Neutron activation analysis

The activities of either ^{122}Sb ($t_{1/2} = 67.2 \text{ h}$, $E_\gamma = 0.564 \text{ MeV}$) or ^{124}Sb ($t_{1/2} = 60 \text{ days}$, $E_\gamma = 0.61$ and 1.69 MeV) are measured, often by INAA. The major interferences include ^{76}As ($t_{1/2} = 26.4 \text{ h}$, $E_\gamma = 0.559 \text{ MeV}$). If As is present, a radiochemical separation or a study of decay curves is necessary unless the peak of ^{124}Sb at 1.69 MeV can be counted [32].

Fluorescence

Non-dispersive AFS with atomization in an Ar- H_2 flame offered an ADL of 40 pg [50]. Wavelength dispersive XRF was used for real

samples after the coprecipitation of Sb with $\text{La}(\text{OH})_3$, hydride generation and trapping of the SbH_3 on an impregnated cellulose filter [31]. Laser-excited GF AFS offered an ADL of 20 fg [51]. Use of candoluminescence spectrometry in the range 10–70 ng ml⁻¹ has been reported [20].

14.3 ANALYSIS OF REAL SAMPLES

Antimony is often analyzed in an array of hydride forming elements and several applications (especially for geosamples) are listed in various Tables in Part II. Common sources of error include volatility losses (especially if chloride is present) and contamination from the reagents and irradiation vials used for NAA. Another category of errors is associated with the stability of Sb(III) and Sb(V) spikes (exhaustively discussed [11]) and the uncertainty about the oxidation state in which Sb is actually present. Differentiation between Sb(III) and Sb(V) is often of concern and can be achieved by the choice of experimental conditions for extraction or volatilization [52]. Applications of coupled techniques to speciation of organoantimony compounds are scarce [34].

Water samples

As both Sb(III) and Sb(V) are present in natural waters, a pre-reduction of Sb(V) to Sb(III) is required for total Sb determination [6,32]. Removal of dissolved gases to prevent oxidation of Sb(III) spikes on sea water is essential to obtain good recoveries [3]. A speciation procedure based on the determination of Sb(III) and total Sb after pre-reduction of Sb(V) to Sb(III) by NAA has been developed [32]. Methods for the determination of Sb in water are summarized in Table 14.1.

Geochemical and environmental samples

These are dissolved in *aqua regia* under pressure. Antimony is determined upon volatilization as SbH_3 , usually simultaneously with other hydride forming elements (*cf.* Part II). Digestion of organic sludges has been discussed [54]. Antimony tended to be retained by uncertain mechanisms in the silicate residues, when the samples were digested with a mixture of HNO_3 and HClO_4 . The Sb included in the precipitates could be recovered using HF digestion followed by acid dissolution. Wickbold combustion has been investigated for the decomposition of various environmental CRMs for Sb determination [55]. A complex procedure based on the extraction of Sb with xanthate and volatilization as SbH_3 has been developed [56].

TABLE 14.1

Determination of antimony in water

Water sample (amount)	Separation and/or preconcentration	Detection technique	DL (ng/ml)	Ref.
CRM (10 ml)	volatilization as SbH_3	ICP MS	2.4	49
CRM	volatilization as SbH_3	FI ICP MS	1–4	53
CRM sea (5 ml)	volatilization as SbH_3 , trapping in a GF	GF AAS	40	4
Potable, surface (5 ml)	volatilization as SbH_3	FI GF AAS	5	6
Waste	volatilization as SbH_3	ICP AES	0.19	2
Sea (100 ml)	volatilization as SbH_3	QF AAS	7 ^a	9
Sea, lake, ground water	coprecipitation with thioanilide	NAA	few	32
Lake, river	volatilization as SbH_3	QF AAS	1–10	3

a Absolute detection limit, pg.

Biological samples

The Sb level in serum (*ca.* 0.5–1 ng ml⁻¹) is accessible practically only by NAA. The application of direct GF AAS is hampered by the need for dilution degrading the detection limits [41]. Sample digestion was recommended [41]. Urine was analyzed by GF AAS using a pyrocoated graphite tube with a L'vov platform and Ni matrix modifier without the need for digestion [41]. Alternatively, urine samples have been digested and cleaned up on an Amberlite IR-120 column [25]. Urine Sb can be extracted by APDC either directly [20] or upon digestion [25]. Aspects of precision and accuracy in NAA of biosamples have been discussed [57]. Yield of hydride generation is strongly sample dependent and should be determined for virtually each sample [57]. Methods for the determination of Sb in biomaterials are summarized in Table 14.2.

Industrial materials

Industrial materials are analyzed for Sb on sample dissolution and volatilization of SbH_3 (Table 14.3) by a variety of instrumental techniques.

TABLE 14.2

Determination of antimony in biological materials

Sample (amount)	Digestion	Separation and/or preconcentration	Detection technique	DL ($\mu\text{g/g}$)	Ref.
Blood, urine (2.5 ml)	$\text{HNO}_3\text{--HClO}_4\text{--H}_2\text{SO}_4$	none	GF AAS	n.g.	41
Urine (10 ml)	none	extraction with APDC (MIBK)	CL	n.g.	20
Urine (100–200 ml)	$\text{HNO}_3\text{--HClO}_4\text{--H}_2\text{SO}_4$	extraction with APDC (MIBK)	GF AAS	10^a	25
Breast tissue	<i>aqua regia</i> – HClO_4	extraction with PAR (benzene) after separation of Se	RNAA		58
CRM plant (1 g)	$\text{HNO}_3, \text{HClO}_4$	coprecipitation with $\text{La}(\text{OH})_3$, volatilization as SbH_3	XRF	0.03	31
CRM plant (0.5 g)	dry ashing with $\text{MgO--Mg}(\text{NO}_3)_2$, dissolution in H_2SO_4	volatilization as SbH_3	QF AAS	260^a	15
Mosquito larvae	$\text{HNO}_3\text{--HClO}_4\text{--H}_2\text{SO}_4\text{--N}_2\text{H}_4$	none	GF AAS	n.g.	41

^a Absolute detection limit, pg.

CL = candoluminescence.

Flame AAS determination of Sb in PVC samples on dissolution in $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ has been reported [61,62]. In the analysis of silicon by GF AAS, solid sampling led to less precise results (owing to the inhomogeneity of samples) and to erosion of the GF (owing to the formation of SiC) [63].

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TABLE 14.3

Determination of antimony in industrial materials

Sample (amount)	Dissolution	Separation and/or preconcentration	Detection technique	DL (ng/g)	Ref.
Copper (1 g)	HNO ₃ -H ₂ SO ₄	coprecipitation with La(OH) ₃	ID ICP MS	5	30
Copper (0.5 g)	HNO ₃	volatilization as SbH ₃	ICP AES	0.19 ^a	2
Copper (0.1 g)	HCl-HNO ₃	volatilization as SbH ₃	ICP AES		5
CRM steel (0.1 g)	H ₂ SO ₄	volatilization as SbH ₃	QF AAS	0.26 ^b	15
CRM steel, iron (0.5 g)	<i>aqua regia</i> - H ₂ SO ₄	none	ICP AES	8 ^a	48
Polyester films (2-3 g)	ashing with Mg(NO ₃) ₂ , dissolution in H ₂ SO ₄	volatilization as SbH ₃	FAAS	0.62 ^b	8
Electrodes from lead-acid cells	oxidation with NaClO, HNO ₃ - tartaric acid	extraction with DDTC (MIBK)	FAAS		22
Lead and zinc concentrates (0.1-1 g)	H ₂ SO ₄ -K ₂ S ₂ O ₇	extraction as SbCl ₅ (<i>n</i> -butyl acetate)	FAAS		19
Gold (0.25 g)	<i>aqua regia</i>	matrix precipitation as Au ⁰	GF AAS		59
Selenium (0.05 g)	HNO ₃	matrix precipitation as Se ⁰	GF AAS		60
PVC (0.1 g)	H ₂ SO ₄ -H ₂ O ₂	volatn. as SbH ₃	FAAS	n.g.	1

a In the solution fed, ng/ml; ^b Absolute detection limit, ng.

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Arsenic

Arsenic (atomic weight 74.92) is a metalloid which exists in three allotropic forms. The most stable one, grey arsenic, has a density of 5.73 g cm^{-3} and sublimes at 604°C . Arsenic occurs in the earth's crust with an average abundance of *ca* 3 ppm, mostly as arsenopyrite (FeAsS), and accompanies Co, Cu and Pb ores. The need for trace determination of As results from the environmental concerns through human use of pesticides, non-ferrous smelters and coal-fired power plants. Trace As has an adverse effect on the mechanical properties of steel. Arsenic can be used therapeutically but at higher concentrations it becomes toxic. The toxicity strongly depends on the speciation. Some forms of As (arsine, arsenite) are highly toxic whereas others (e.g., cacodylic acid, arsenobetaine) are neutral to living organisms.

Arsenic is commonly encountered in aqueous solutions at two redox states: III (arsenite, AsO_3^{3-}) and V (arsenate, AsO_4^{3-}), which tend to change readily and reversibly. Arsenic(III) forms volatile halides (AsF_3 , AsCl_3 , AsBr_3 , AsI_3). The most common As(–III) compound is gaseous arsenic trihydride (arsine, AsH_3) which is formed in reducing acid media and is a powerful reductor itself. There exists a variety of organoarsenic(–III) stable compounds which are summarized in Table 15.1.

15.1 SEPARATION AND PRECONCENTRATION

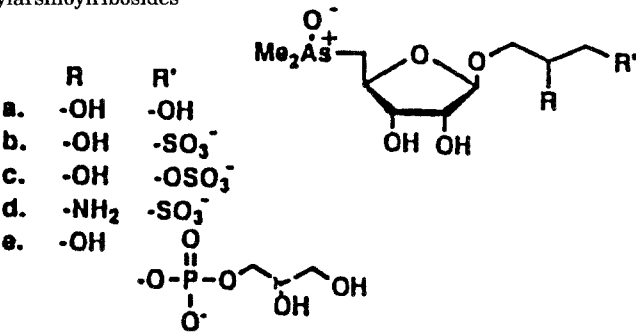
Volatilization

Both As(III) and As(V) react with NaBH_4 in acidic solution to produce AsH_3 , but at different rates. The resulting difference in sensitivity between As(III) and As(V) can be levelled by optimization of operating parameters [1,2], trapping the hydrides formed prior to determination

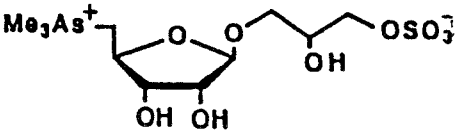
TABLE 15.1

Arsenic species encountered in biological or environmental samples [123]

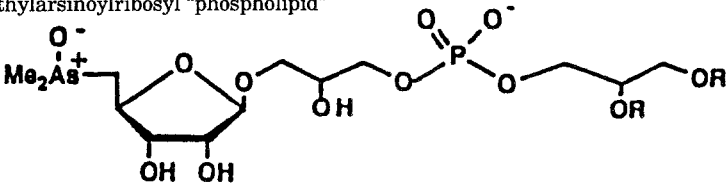
Arsenic(III)	AsO_3^{3-}
Arsenic(V)	AsO_4^{3-}
Dimethylarsenic acid (DMA)	$\text{Me}_2\text{AsO}_2\text{H}$
Methylarsenic acid (MMA)	MeAsO_3H_2
Trimethylarsine	Me_3As
Trimethylarsine oxide (TMAO)	$\text{Me}_2\text{As}^+\text{O}^-$
Tetramethylarsonium ion	Me_4As^+
Arsenobetaine (trimethylarsonioacetate)	$\text{Me}_3\text{As}^+\text{CH}_2\text{COO}^-$
Arsenocholine (2-trimethylarsonioethanol)	$\text{Me}_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$
Dimethylarsinoylethanol	$\text{Me}_2\text{As}^+(\text{O})\text{CH}_2\text{CH}_2\text{OH}$
Dimethylarsinoylribosides	



Trimethylarsonioriboside “sulphate ester”



Dimethylarsinoylribosyl “phospholipid”



R= palmitoyl

[3–10] or converting all As either to As(III) or As(V). Arsine can be trapped cryogenically [3,4], in a graphite furnace for AAS [5,6,11] and MIP AES [7] determination, or chemically in a solution of AgDDTC [8] or iodine [9,10]. Reaction media for selective reduction of various arsenic species have been exhaustively discussed based on a literature survey [12]. Potassium iodide in fairly concentrated HCl solution is the most common reductant used [13–18,19]. The reaction is fairly slow; up to 1 h is required for quantitative reduction [3,20]. Identical responses cannot be obtained from arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid at the same conditions. The mixture of KI with NH_2OH [18] or ascorbic acid [11] is more effective. L-cysteine was found to be especially suitable since it can not only reduce As(V) to As(III) at moderate acidities [21–23,24] but also organoarsenic compounds [25]. Electrochemical reduction was reported [14]. Oxidation to As(V) is less popular as it is slower but is often the choice whenever oxidative digestion of the sample precedes the determination step [26–28]. The AsH_3 generation is interfered with by other hydride-forming elements (Te, Se, Sn, Pb, Hg), transition metals (Ni, Ag, Zn, Cu, Co, Mo, Au, Pd) [12,29–31] and oxidizing ions ($\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , NO_3^-) [30,32]. Antimony, Bi and Fe interfere with As(III) but do not affect As(V); Zn has the opposite effect [30]. The mechanisms of the interference have been discussed [33,34] with emphasis on Cu, Co and Ni [35]. The interferences can be removed by masking with EDTA [12,15], L-cysteine [21–23,36] (at the expense of increase in Se and Te interference) [23], 1,10-phenanthroline [12,37,38], thiourea (for Cu) [12,32] and thiosemicarbazide [17]. Oxidizing ions should be prereduced, e.g. with ascorbic acid, whereas sulphide should be preoxidized [32]. An alternative approach is initial separation of As from the interfering elements. Arsine was generated *on line* on a strong anion-exchange resin in a BH_4^- form [36]. A method for volatilization of As as AsCl_3 was developed to improve the tolerance toward transition metals in comparison with hydride generation [42,43].

Extraction

Arsenic (III) can be selectively extracted from acidic media (pH 1–4.5) with APDC into CHCl_3 in the presence of EDTA [44,45] and back-extracted into HNO_3 [45]. Arsenic(III) can be extracted as AsCl_3 [28], AsI_3 [31], xanthate [17] or dithiocarbamate [46]. The extraction of As(V)–APDC is not recommended owing to the formation of gaseous products of APDC and pyrrolidine [37] reduction in the organic phase. Back-ex-

traction is often not valid for arseno-amido derivatives which are more soluble in CHCl_3 than in water [37]. To be extracted As(V) needs to be reduced, *e.g.* by thiosulphate [45], hydrazine [28] or Ti(III) [17,46].

Coprecipitation

Arsenic (III) can be precipitated as As_2S_3 [47], by dibenzylthiocarbamate [48–50] or APDC with Ni carrier [51]. Arsenic(V) can be precipitated on $\text{Fe}(\text{OH})_3$ [49] or $\text{La}(\text{OH})_3$ [52] or as the molybdate complex with TPP [50] or Pe_4N^+ [53]. Reduction to the elemental As by hypophosphorous acid [54] or by SnCl_2 [55] with Cu, Se or Te as carrier was successful. The molybdoarsenate complex can be preconcentrated by flotation as an ion pair with Malachite Green; phosphate interferes [56].

15.2. DETERMINATION TECHNIQUES

Spectrophotometry

The arsenomolybdenum blue method is the most widely used. Arsenic(V) is reacted with $(\text{NH}_4)_2\text{MoO}_4$ to form a colourless molybdoarsenic heteropolyacid. The latter is then reduced (with SnCl_2 or hydrazine) to arsenomolybdenum blue the absorbance of which is measured in the aqueous phase or on extraction ($\epsilon = 2.5 \times 10^4$ at 730 nm). Methods based on ion associates of molybdoarsenate with basic dyes are more sensitive [57].

Flame atomic absorption spectrometry

The EDL is advantageous over the HCL in terms of sensitivity. An air– C_2H_2 -rich reducing flame gives a sensitivity of $1 \mu\text{g ml}^{-1}$ at the most sensitive 189.0 nm and 193.7 nm lines. A severe background interference occurs which can be alleviated with N_2O – C_2H_2 flame at the expense of a 50% loss in sensitivity. A sample with a total salt content greater than 1% will produce apparent absorption at the 193.7 line. Background correction is indispensable. Separation of As by hydride generation is the basic approach.

Quartz furnace atomic absorption spectrometry

Flame or electrothermally heated quartz tube AAS is used for the determination of AsH_3 , often in a flow-injection mode. The effect of atomizer design, purge hydrogen flow rate and atomizer temperature on the sensitivity has been investigated [58]. Radiotracers ($\text{As}(\text{III})$,

As(V), MMAA, DMAA) have been used for examination of gas-liquid separators for HG-AAS [59].

Graphite furnace atomic absorption spectrometry

This technique offers a DL of 50 ng ml^{-1} (characteristic mass of 15 pg). A successful determination is challenged by the volatility of As_4O_6 , which is likely to be lost at relatively low temperatures [60] and the variety of the existing As species which have different volatilities. The use of a matrix modifier is mandatory; the most widely used ones include: $\text{Ni}(\text{NO}_3)_2$ [5,10,61–63], Ni-ascorbic acid [64], $\text{Ni-Mg}(\text{NO}_3)_2$ [65,66], Pd [5,11,46,67,68], $\text{Pd}(\text{NO}_3)_2\text{-Mg}(\text{NO}_3)_2$ [69,70], $\text{PdCl}_2\text{-K}_2\text{S}_2\text{O}_8$ [71]. Equal sensitivities were obtained for the inorganic and all the organic species by using the conventional STPF furnace programme. The fast programme is effective only if a matrix modifier is used [72]. Enhancement of sensitivity was reported by using a graphite cloth ribbon [73]. Arsine can be trapped in a graphite furnace at $400\text{--}600^\circ\text{C}$ [6,74] and subsequently atomized. Spectral interferences in GF AAS include Ca and Mg phosphates and require effective background correction, using D_2 [67], Zeeman [5,63,65,75], or Smith-Hieftje [66] methods. The interference of sulphate is alleviated by thiourea [46]. Spectral interferences from Al in GF AAS at the 193.7 nm line are the major problem [76]. Cobalt and Fe may interfere at the 197.2 nm line [77]. The Al interference can be resolved mathematically [76]. Interferences in GF AAS have been exhaustively discussed [77]. Slurry GF AAS was applied to the determination of As in Fe(III) oxide pigment [78], whole coal [68] and dry-ashed beer [64]. Calibration with aqueous standards was possible provided that a matrix modifier was used and background correction applied.

Inductively coupled plasma atomic emission spectrometry

The most sensitive lines, 189.042, 193.7 and 228.812 nm, offer moderate detection limits of $35\text{--}50 \text{ ng ml}^{-1}$. Aluminium interferes on the 189.042, 193.759 and 197.262 nm lines, Cr on the 189.042 and 193.759 nm lines, Co on the 197.262 and 228.812 nm lines, V on the 189.042, 193.759, 197.262 and 228.812 nm lines and Cd on the 228.812 nm line. To alleviate spectral interferences As is introduced into the ICP [31,61, 79–81], DCP [2,21–23,38] or MIP [82] as AsH_3 . Detection limits in *on-line* mode are *ca* 1 ng ml^{-1} . A graphite furnace was used for *in-situ* concentration of AsH_3 followed by its vaporization into an MIP [7].

Mass spectrometry

Arsenic has only one stable isotope, ^{75}As , which prevents isotope dilution analysis. ICP MS is interfered with in chloride media by the polyatomic ion $^{40}\text{Ar}^{35}\text{Cl}^+$. This interference can be efficiently reduced by addition of N_2 (ca 2%) to the Ar nebulizer gas [83–86]. Other methods have included a mathematical correction based on the $^{40}\text{Ar}^{37}\text{Cl}^+$ signal [87], chromatographic separation of the As and Cl [88–91], addition of propan-2-ol [84] or EtOH [92] to suppress the formation of ArCl^+ or pre-separation of As by hydride generation [13,93] or *on line* ASV [94].

Neutron activation analysis

The NAA determination of arsenic is based on the γ -counting of the ^{76}As ($t_{1/2} = 26.4$ h) nuclide. A detection limit at the low ng level can be obtained in the absence of matrix, otherwise a radiochemical separation is necessary. Ion exchange [47], extraction [45] and precipitation [48,47, 50] have been used. Apart from Na and Br, Sb interferes [62]. Yield of hydride generation is strongly sample dependent and should be determined for virtually each sample [95].

Fluorescence techniques

Non-dispersive AFS with atomization of AsH_3 in a H_2 -Ar flame offers a sensitivity of 0.1 ng and excellent reproducibility [96]. Both ED [49] and WD [54,55,97,98] XRF were applied but required a separation step. Precipitation of As(III) and As(V) with dibenzylthiocarbamate and $\text{Fe}(\text{OH})_3$ or coprecipitation with Se [55], Te [54] or La [98] carriers enables detection limits down to $0.1 \mu\text{g g}^{-1}$ to be obtained. Trapping of AsH_3 onto an impregnated cellulose filter has been proposed [98]. Laser excited AFS of As with DLs 54 fg has been reported [99].

15.3 ANALYSIS OF REAL SAMPLES

15.3.1 Environmental and geological materials

Air

A standard method for determining As in workplace air using HG AAS has been proposed. The method involves sampling air by drawing it through a membrane filter with a paper backup pad, both of which have been treated with Na_2CO_3 solution. Particulate As compounds and As(III) oxide vapour were collected but not arsine. The filter and pad

were digested with $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--H}_2\text{O}_2$ prior to hydride generation [100].

Geological samples

Ores require an oxidizing attack with $\text{HNO}_3\text{--Br}_2$ [17,46] or $\text{HNO}_3\text{--HClO}_4$ [55] to convert As(III) to As(V) prior to the addition of HF to avoid volatilization of AsF_3 . Pressure bomb digestion with $\text{HNO}_3\text{--HCl}$ [9,20] or $\text{HNO}_3\text{--H}_2\text{SO}_4$ [55,101] is usually employed. HF-containing mixtures [61] are seldom used unless a powerful oxidant, e.g. KMnO_4 is added. About 10% of As can be lost during *aqua regia* digestion [102]. Ten digestion methods have been compared for the As determination in soils [101], the best results were obtained with $\text{HNO}_3\text{--H}_2\text{SO}_4$ leaching procedure. Leaching with HCl was found to be suitable for inorganic As [62]. Acid leaching of slurries of soil, sludge, incinerator ash, and coal fly ash was found to give recoveries similar to those obtained by the *aqua regia* method [102]. Wickbold combustion has been investigated for the decomposition of various environmental CRMs [103]. The majority of determination techniques are preceded by hydride generation. Heavy metals in the sample can lead to severe depression of the absorbance signal so standard addition correction is recommended [102]. A detailed scheme for speciation of As in contaminated soil and river sediment by sequential leaching has been proposed [104]. Analytical methods for the determination of total As are summarized in Table 15.2.

Waters

Analytical methods are summarized in Table 15.3. Arsenic is usually determined on hydride generation. The sensitivity is often improved by cryogenic trapping [4]. The HG methods have a drawback that non-hydride-forming species (up to 15–20%) remain undetected [110]. This is not corrected by the standard addition albeit the latter is essential to correct for transition metals interferences. Total arsenic analysis requires either dry ashing [110] or combined $\text{H}_2\text{O}_2\text{--HNO}_3$ and UV oxidative digestion [5].

15.3.2 Biological samples

Analytical methods for the determination of As in biological samples are summarized in Table 15.4.

TABLE 15.2

Analytical methods for the determination of arsenic in geochemical materials

Samples (amount)	Dissolution	Separation/ preconcentration	Detection	Detection limit (µg/g)	Ref.
CRMs (0.5 g)	<i>aqua regia</i> (bomb)	volatn. as AsH ₃	FI AFS	0.1 ^a	96
CRM soils (0.5–1 g)	HNO ₃ , HClO ₄ – H ₂ SO ₄ (micro- wave assisted)	volatn. as AsH ₃	QF AAS	n.g.	105
Soils (0.5 g)	HNO ₃ –H ₂ SO ₄	volatn. as AsH ₃	QF AAS	n.g.	101
CRM soil (0.3 g)	HNO ₃ –HCl (bomb)	volatn. as AsH ₃ , trapping in a Ce(IV)–KI soln.	GF AAS	0.02 ^a	9
CRM sediments (0.1–0.2 g)	HNO ₃ –HClO ₄ – HF (bomb)	none	ICP AES	5.0	61
CRM sediments (0.5 g)	HNO ₃ –HClO ₄ – HF	volatn. as AsH ₃ , ICP AES	2.5	61	
CRM sediments (0.1–0.2 g)	HNO ₃ –HClO ₄ – HF (bomb)	none	GF AAS	0.5–1.0	61
Sediments (0.5–0.7 g)	HCl leaching	anion-exchange	GF AAS	0.5	28
CRM rocks, ores, soils, sediments (1 g)	HNO ₃ –Br ₂ , HCl–HClO ₄ , HF	extrn. as xanthate (cyclohexane), stripping (HCl)	GF AAS	0.2	46
CRM rocks, ores, soils, sediments (1 g)	HNO ₃ –Br ₂ , HCl–HClO ₄ , HF	extrn. as xanthate (cyclohexane), stripping (H ₂ O ₂), volatn. as AsH ₃	QF AAS	0.1	17
Rocks (0.5–1 g)	HNO ₃ –HClO ₄ , HClO ₄ –HF	pptn. with Se	XRF	0.6	55
Stream sediment (1 g)	HNO ₃	volatn. as AsH ₃	QF AAS	n.g.	106
CRM sediment (0.1–0.5 g)	HNO ₃ –HCl (bomb)	volatn. as AsH ₃	FI FAAS	n.g.	20

^a Absolute detection limit, ng.

TABLE 15.3

Analytical methods for the determination of arsenic in water

Water (amount)	Separation/ preconcentration	Detection	Detection limit (ng/ml)	Ref.
CRM	volatn. as AsH_3 , membrane sepn.	ICP MS	0.5	13
CRM (10 ml)	volatn. as AsH_3	ICP MS	1.5	93
CRM surface (100 ml)	pptn. with DBDTC	NAA	0.02	48
CRM sea (10 ml)	volatn. as AsH_3 , trapping in a GF	MIP AES	0.012	7
CRM sea (0.5 ml)	volatn. as AsH_3 , trapping in a GF	GF AAS	0.060	6
Sea (200–500 ml)	pptn. with Se	XRF	1	55
Sea (300 ml)	extrn. with APDC (CHCl_3), digestion with HNO_3 – HClO_4 , volatn. as AsH_3	QF AAS	0.03	44
Sea, river, mine (100 ml)	extrn. with APDC (CHCl_3), back-extrn. into HNO_3	NAA	0.01	45
Surface, coastal (100 ml)	pptn. of As(V)-molybdate with TPhP.Cl	NAA	n.g.	50
Surface, coastal (100 ml)	pptn. of As(III) with DBDTC	NAA	n.g.	50
River	volatn. as AsH_3	QF AAS	0.6	26
River water (0.25–0.5 l)	volatn. as AsH_3	QF AAS	5	107
Drinking (5 ml)	volatn. as AsH_3	DCP AES	0.6	21,23
Drinking, mineral (10 ml)	volatn. as AsH_3	FI FAAS	n.g.	20
Mineral (50 ml)	volatn. as AsH_3 , trapping in a Ce(IV)-KI soln.	GF AAS	0.06	9
Mineral (5–25 ml)	volatn. as AsH_3	AAS	20	11
Spring (100 ml)	pptn. of As(V)-molybdate with TPpP.Br	ICP AES	0.3	53
Ground (1 l)	copptn. of As(III and V) on $\text{Th}(\text{OH})_4$, volatn. as AsH_3	VIS	n.g.	108
Waste	sorption of As(V) on Oc_2SnCl_2 modified support; elution with 2 M HCl	FAAS GF AAS	10	109

TABLE 15.4

Analytical methods for the determination of arsenic in biological materials

Sample (amount)	Decomposition	Separation/pre- concentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Mussel (0.25 g)	$\text{HNO}_3\text{--H}_2\text{O}_2$ (microwave assisted)	none	GF AAS	n.g.	111
Mussel (0.25 g)	dry ashing [$\text{MgO--Mg(NO}_3)_2$]	volatn. as AsH_3	QF AAS	0.02	112
Mussel (10 g wet)	dry ashing [$\text{MgO--Mg(NO}_3)_2$]	none	ICP AES	0.1	112
Marine CRMs (0.5 g)	dry ashing [$\text{Mg(NO}_3)_2$]	volatn. as AsH_3 , trapping in a GF	GF AAS	0.15	6
Marine CRMs (0.3–0.4 g)	$\text{HNO}_3\text{--HClO}_4$ (bomb)	none	ICP AES	5.0	61
Marine CRMs (0.5 g)	$\text{HNO}_3\text{--HClO}_4$	volatn. as AsH_3	ICP AES	2.5	61
Marine CRMs (0.3–0.4 g)	$\text{HNO}_3\text{--HClO}_4$ (bomb)	none	GF AAS	0.5–1	61
Marine CRMs (0.5 g)	HNO_3 , dry ashing [$\text{Mg(NO}_3)_2$]	volatn. as AsH_3	QF AAS	0.06	27
Marine CRMs, eggs, duck liver (0.5 g)	$\text{HNO}_3\text{--H}_2\text{O}_2$	none	GF AAS	n.g.	75
Marine CRMs (10 g)	dry ashing, dissoln. in HCl	none	ICP AES	0.1	113
Marine CRMs (1 g)	HNO_3	none	GF AAS	n.g.	114
Marine (1 g)	$\text{HNO}_3\text{--HClO}_4\text{--}$ H_2SO_4 (bomb)	volatn. as AsH_3	AAS	0.3	25
Mangrove leaves (0.2–0.3 g)	$\text{HNO}_3\text{--HClO}_4$	volatn. as AsH_3	FAAS	0.45 ^a	14
Plant CRMs (0.2 g)	$\text{HNO}_3\text{--H}_2\text{O}_2$	extrn. as AsI_3 , volatn. as AsH_3	ICP AES	0.7 ^a	31
Plant (1 g)	$\text{HNO}_3\text{--HClO}_4$	volatn. as AsH_3 , trapping in a Ce(IV)-KI soln.	GF AAS	0.02 ^b	9

Sample (amount)	Decomposition	Separation/pre- concentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Plant CRMs (0.5 g)	$\text{HNO}_3\text{--HClO}_4$, HF	evaporation, volatn. as AsH_3	MECA	10^b	15
Plant CRMs (0.07 g)	dry ashing [$\text{MgO--Mg(NO}_3)_2$]	volatn. as AsH_3	QF AAS	0.2^b	32
Plant CRMs (0.5 g)	$\text{H}_2\text{SO}_4\text{--HNO}_3\text{--}$ (NH_4) $_2\text{C}_2\text{O}_4$	volatn. as AsH_3	QF AAS	0.02^b	1
Plant CRMs, human hair (0.5–1.0 g)	HNO_3	volatn. as AsH_3	DCP AES	300^a	38
Plant CRMs (5 g)	dry ashing [$\text{MgO--Mg(NO}_3)_2$]	volatn. as AsH_3	FAAS		18
BioCRMs (0.25 g)	$\text{H}_2\text{SO}_4\text{--HNO}_3$	volatn. as AsH_3	GF AAS	0.2^a	3
BioCRMs (1 g)	HNO_3 , HClO_4	copptn. with La, volatn. as AsH_3	WD XRF	0.1	98
BioCRMs (0.3 g)	HNO_3 , H_2SO_4 and HClO_4	volatn. as AsH_3 , liquid N_2 trapping	QF AAS	6^b	4
Biomaterials (0.25 g)	$\text{H}_2\text{SO}_4\text{--HClO}_4$	volatn. as AsH_3	QF AAS	5^a	107
Food CRMs (5 g)	HNO_3 , dry ashing (MgO)	pptn. with APDC	GF AAS	10	51
Food CRMs (5 g)	$\text{HNO}_3\text{--HClO}_4\text{--}$ H_2SO_4	volatn. as AsH_3	QF AAS	n.g.	19
Food (5 g)	$\text{HNO}_3\text{--HClO}_4\text{--}$ H_2SO_4	volatn. as AsH_3	FAAS	n.g.	28
Food (10 g)	leaching: $\text{HClO}_4\text{--}$ $\text{Fe}_2(\text{SO}_4)_3$	extrn. of AsCl_3 (CHCl_3)	FAAS	n.g.	28
Food (1 g)	HCl--KI (microwave assisted)	volatn. as AsCl_3	QF AAS	0.07	115
Blood (0.5 ml)	HNO_3	volatn. as AsH_3	QF AAS	0.2^a	24
CRM urine (25 ml)	none	electrolysis	ICP MS	1^a	94
Herbage (1 g)	HNO_3 , $\text{Mg(NO}_3)_2\text{--}$ $\text{Ni(NO}_3)_2$	pptn. with a Te carrier	WD XRF	100^b	54
Beer (50 g)	dry: $\text{Mg(NO}_3)_2\text{--}$ MgO	volatn. as AsH_3	QF AAS	0.0001	16

^a ng/ml in the analyzed solution; ^b absolute detection limit, ng.

Blood and serum

Blood and serum show the normal As level of 1 ng ml^{-1} . Direct GF AAS analysis on dilution to decrease chloride concentration, deproteinization with HNO_3 , matrix modification with Ni and Zeeman background correction are favoured [116,117]. The chloride interference from the whole blood in ICP MS was suppressed by the addition of propan-2-ol [84].

Urine

GF AAS with Zeeman background correction and Ni–Mg nitrate gives a DL of *ca* 10 ng ml^{-1} in undiluted urine [65]. Dilution is necessary to minimize the chloride interference [65]. The precipitation of the chloride as AgCl was not suitable [88]. Phosphate and sulphate interfere but there is no interference from other major urine matrix constituents such as CaCl_2 , MgCl_2 , NaCl , urea, creatinine and albumine [118]. A mixture of $\text{Ni}(\text{NO}_3)_2$ – $\text{Mg}(\text{NO}_3)_2$ – PdCl_2 – $\text{K}_2\text{S}_2\text{O}_8$ was used for the modification of urine to give quantitative recoveries of As(III), As(V), MMA, DMA and arsanilic acid [71]. Arsenic was determined in urine by ICP MS using the addition of about 2% N_2 to the Ar nebulizer gas to reduce the chloride interference [83,85]. Digestion of urine using HNO_3 – H_2SO_4 – H_2O_2 for total As determination has been recommended [119]. Only microwave digestion with $\text{K}_2\text{S}_2\text{O}_8$ and NaOH can decompose all organoarsenic compounds including arsenobetaine [120].

Marine samples

These contain As as organoarsenic compounds (e.g. arsenobetaine) which require very harsh conditions to be destroyed. Direct analysis of biological tissues using an inner cup solid sampling technique, Zeeman correction and Ni matrix modifier in an HNO_3 – H_2SO_4 mixture has been reported [121]. Hydride generation techniques require As to be present as either As(III) or As(V) so a sample digestion is required [25]. Arsenic(III and V) can be leached with dilute HClO_4 at 80°C in the presence of a mild oxidant (e.g. ferric sulphate) [28]. Dry ashing with $\text{Mg}(\text{NO}_3)_2$ – MgO as a volatilization inhibitor was reported to be successful for the destruction of marine [6,112] and plant [16,18,32] tissues. Combustion in a stream of oxygen gives quantitative recoveries for marine organisms but is slow [25]. Nitric acid alone does not allow for efficient destruction of some As compounds in marine tissues [25]. The complete oxidation of organoarsenic compounds requires addition of H_2SO_4 [28], HClO_4 – H_2SO_4 [25] or $\text{K}_2\text{S}_2\text{O}_8$ [71]. Digestion with a mixture of HNO_3 –

H₂O₂ in sealed tubes [75] or microwave-heated pressure bombs [111] provides an efficient alternative. During this treatment arsenic is oxidized to As(V) [38]. The use of SFE for the recovery of As from dogfish muscle has been discussed [122].

Graphite furnace AAS is the most popular determination technique. Arsenic can be determined without interference at 197.2 nm with the D₂ correction or at 193.7 with the Zeeman system [123]. The D₂ correction is disturbed by Ca and Mg phosphates and is sometimes insufficient despite the Ni(NO₃)₂ matrix modification [114]. The Zeeman correction in combination with the STPF concept is preferred [75,111,114]. Non-spectral interferences may remain [111,114] so the standard additions method should be employed [111]. ICP AES offers freedom from interferences at the As levels higher than 0.1 µg g⁻¹. For samples with lower As levels HG QF AAS has been recommended [112]. Atomic spectrometric analysis for As in foodstuffs has been reviewed [124]. Various techniques have been compared for the analysis of mussels [112]. Results of an interlaboratory collaborative study on the determination of diagnostic levels of As in animal tissue have been presented [125]. Arsenic speciation in clams has been comprehensively discussed [126].

15.3.3 Industrial materials

Methods for the determination of As in industrial materials are summarized in Table 15.5. Arsenic is usually determined by HG AAS or HG ICP AES either directly or after the matrix removal. Arsine generation in the presence of an Se matrix requires oxidation of Se with KMnO₄ to Se(VI) (which is not reducible by NaBH₄) [106] and reduction of Se to Se⁰ by hydrazine [136,137]. The latter method has the advantage of converting all the As present to As(III) which gives better sensitivity than As(V) in HG AAS determination [136]. Results of an interlaboratory exercise on the determination of As in preservative treated timber have been presented [138].

15.4 SPECIATION

The strong species dependence of the toxicity makes speciation analysis of As in environmental and biomedical matrices essential. The two principal approaches include “operational speciation” based on selective extraction, sorption, precipitation or solubilization of particu-

TABLE 15.5

Analytical methods for the determination of arsenic in industrial materials

Sample (amount)	Dissolution	Separation/pre- concentration	Detection	DL ($\mu\text{g/g}$)	Ref.
CRM steel (0.03 g)	H_2SO_4	volatn. as AsH_3	QF AAS	0.22 ^a	32
CRM steel (1 g)	<i>aqua regia</i>	volatn. as AsH_3	QF AAS	0.024 ^a	1
CRM steel (0.5 g)	<i>aqua regia</i>	volatn. as AsH_3	FI FAAS	n.g.	20
CRM steel, iron (0.2–1 g)	HNO_3	volatn. as AsH_3	DCP AES	n.g.	22 23
CRM steel, cast iron (0.1–1 g)	$\text{HNO}_3\text{--HClO}_4$	volatn. as AsH_3 , trapping	QF AAS	1	127
CRM steel (0.5 g)	HCl--HNO_3	volatn. as AsCl_3	FAAS	0.4	43
CRM steel (0.2 g)	$\text{HNO}_3\text{--HClO}_4$	extrn. as molyb- date (MIBK)	GF AAS	n.g.	128
CRM steel (0.1 g)	HCl--HNO_3	volatn. as AsH_3	ICP AES	0.3	129
Steel (0.5 g)	<i>aqua regia--H}_2\text{SO}_4</i>	none	ICP AES	1 ^a	130
Steel (1 g)	$\text{HCl, HNO}_3, \text{H}_2\text{O}_2$	FI HG	AAS		34
Ni-based alloys (1 g)	$\text{HNO}_3\text{--HF}$, microwave assisted	cation exchange re- moval of Ni, volatn. as AsH_3	FI FAAS	4 ^b	39
Ni-based alloys (1 g)	$\text{HNO}_3\text{--HF}$, microwave assisted	cation exchange re- moval of Ni, volatn. as AsH_3	FI FAAS	1.3 ^a	40
Alloys (CRMs) (0.1 g)	$\text{HCl--H}_2\text{O}_2$	extrn. of AsI_3 (xylene), volatn. as AsH_3	ICP AES	0.7 ^b	31
Copper	<i>aqua regia</i>	pptn. of CuI and PbI_2 ; volatn. as AsH_3	FI QF AAS	1 ^b	131
Copper (1 g)	HNO_3	volatn. as AsH_3	QF AAS		34
Copper (2 g)	HNO_3	volatn. as AsH_3	GF AAS	n.g.	129
Copper metal	n.g.	electrolytic matrix removal, volatn. as AsH_3	FAAS	300 ^a	30

Sample (amount)	Dissolution	Separation/pre- concentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Gold (0.25 g)	<i>aqua regia</i>	matrix reduction with hydrazine	GF AAS	n.g.	132
Selenium (0.5 g)	HNO_3	matrix reduction with hydrazine	GF AAS	n.g.	46
Selenium (0.1 g)	HNO_3	volatn. as AsH_3	QF AAS	n.g.	106
Silicon (1 g)	$\text{HNO}_3\text{--HF--H}_2\text{O}_2$	none	GF AAS	2 ^b	63
Silicon (1 g)	$\text{HNO}_3\text{--HF--H}_2\text{O}_2$	volatn. as AsH_3	FAAS, DCP AES	n.g.	63
Cu concentrate, U tailings (CRMs) (1 g)	$\text{HNO}_3\text{--Br}_2$, HCl--HClO_4 , HF	extrn. as xanthate (cyclohexane), stripping (HCl)	GF AAS	0.2	46
Cu concentrate, U tailings (CRMs) (1 g)	$\text{HNO}_3\text{--Br}_2$, HCl--HClO_4 , HF	extrn. as xanthate (cyclohexane), stripping (H_2O), volatn. as AsH_3	QF AAS	0.1	17
Food-grade H_3PO_4	dil. with H_2O	none	GF AAS	n.g.	67
Hydrofluoric acid (1 ml)	none	evaporation, volatn. as AsH_3	QF AAS	0.25 ^b	133
CRM glasses, catalysts (0.1 g)	HF (microwave assisted)	none	GF AAS	10	134
Butter (1 g), polymers (0.6 g)	oxygen bomb, $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--HClO}_4$	volatn. as AsH_3	GF AAS	0.005	7 41 64
Coal (0.7 g)	HClO_4	copptn. with La, volatn. as AsH_3	AAS	0.06	52
Coal (0.7 g)	HClO_4	copptn. with La	AFS	0.025	52
Glass, sand	$\text{HF--H}_2\text{SO}_4\text{--KMnO}_4$	extrn. as AsCl_3 (toluene), back- extrn. (H_2O), volatn. as AsH_3	QF AAS	0.05	135
Glycerine	dil. with water	volatn. as AsH_3	ICP AES	n.g.	79

^a Absolute detection limit, ng; ^b in the analyzed solution, ng/ml.

lar forms [16,62,104,126,139] and “virtual speciation” based on chromatographic separation of arsenic species followed by their *on-line* detection. Speciation of As has been reviewed [140]. Methods for speciation analysis using LC and GC based techniques are summarized in Tables 15.6 and 15.7, respectively.

TABLE 15.6

LC-based methods for speciation analysis of organoarsenic compounds

Analyte	Separation mode	Detection	Sample	Ref.
As(III), MMA, DMA, As(V)	anion exchange	FAAS	urine	141
As(III), MMA, As(V)	anion exchange	HG QF AAS	soil pore water	144
As(III), MMA, DMA, As(V)	anion exchange	ICP MS	seafood	145
As(III), MMA, DMA, As(V)	anion exchange	AAS	urine	146
As(III), MMA, DMA, As(V)	anion exchange	ICP MS	urine	147 148
As(III), MMA, DMA, As(V)	anion exchange	ICP AES	mineral water	149
As(III), MMA, DMA, As(V)	anion exchange	ICP MS	urine, club soda, wine	150
As(III), MMA, DMA, As(V), phenylarsonic acid, triphenylarsine oxide	anion exchange	ICP AES	cultured cell suspension	151
As(III), MMA, DMA, As(V)	anion exchange	ICP AES	artificial fish extract	152
As(III), MMA, DMA, As(V)	anion exchange	ICP MS	soil extracts	153
As(III), MMA, DMA, As(V)	anion exchange	HG AAS	pore water	154
As(III), As(V), MMA, DMA, arsenobetaine, arsenocholine	anion exchange	ICP AES	spiked mineral water	155
As(III), As(V), MMA, DMA, arsenobetaine, arsenocholine, p-aminophenylarsenate	anion exchange	GF AAS	spiked lake and river water	156
As(III), As(V), MMA, DMA, arsenobetaine, arsenocholine	anion exchange	ICP MS	artificial fish and sediment extracts	157
As(III), As(V), MMA, DMA, arsenobetaine	anion exchange	GF AAS	clams	158

Analyte	Separation mode	Detection	Sample	Ref.
As(III), As(V), MMA, DMA, arsenobetaine, arsenocholine	anion exchange	HG ICP AES	standards	159
As(III), As(V), MMA, DMA	ion interaction	GF AAS	clams	158
As(III), As(V), DMA	anion exchange	ICP MS	urine	89
Arsenobetaine, arsenocholine	cation exchange	ICP AES	urine	141
Arsenobetaine, arsenocholine, trimethylarsine oxide, tetramethylarsonium, 2-dimethylarsinylethanol, glyceryl-phosphoryl- arsenocholine	cation exchange	ICP MS	seafood	145
Arsenobetaine, arsenocholine TeMA	reversed phase	GF AAS	crabs	158
Arsenobetaine, arylarsonic acids	reversed phase	HG GF AAS	clams	160
As(III), MMA, DMA, As(V)	ion interaction	ICP MS	standards	161
Arsenobetaine	ion interaction	ICP MS	urine	142
As(III), MMA, DMA, As(V)	ion interaction	HG QF AAS	urine	143
As(III), MMA, DMA, As(V)	ion interaction	ICP AES	shale oil	162
As(III), As(V), cacodylate		ACP AES	spiked river and tap water	163
As(III), As(V), MMA, DMA, arsenobetaine		ICP MS	DORM-1	164, 165
15 Organoarsenic species	ion-interaction	ICP MS	DORM-1, DOLT-1	166
4-Hydroxy-3-nitrophenyl-arsonic acid	anion exchange matrix separation, reversed phase	ICP AES	chicken	167
DMA, As(V), arsenosugars	revesed phase	ICP MS	marine tissues	168
As(V), As(III), MMA, DMA, arsenobetaine, arsenocholine	reversed phase	HG AAS	waste water	169
As(III), As(V), DMA, MMA, phenylarsenic acid, arsenocholine, arsenobetaine	capillary zone electrophoresis	UV	standards	170

TABLE 15.7

GC-based methods for speciation of organoarsenic species after derivatization by hydride generation

Analyte	Separation	Detection	Sample	Ref.
As, MMA, DMA	thermal desorption	AAS or ICP AES	standards	171
As, MMA, DMA	thermal desorption	QF AAS	molluscs, algae, river water	172
As, MMA, DMA, TMA, not-hydride-forming organic arsenic	thermal desorption	QF AAS	natural water	173, 174
As, MMA, DMA	packed column GC	AAS	natural waters, seaweed	175
As, MMA, DMA	thermal desorption	QF AAS	reference seawater, river water	176
MMA, DMA, TMAO	packed column GC	AAS	airborne particulate matter	177
As, DMA	packed column GC	QF AAS or MS	artificial seawater (butyltins)	178
As, MMA, MEA, DMA	thermal desorption	QF AAS	tap, lake, river, rain and seawater	179

Arsenic(III), MMA, DMA form volatile hydrides which can be separated by thermal desorption GC or packed column GC. Both As(III) and As(V) form the same hydride AsH_3 so they cannot be determined in one run. Automated speciation of As by HG AAS has been developed; species were resolved on the basis of different sensitivities in various media [180,181]. The more complex arsenic derivatives, arsenobetaine and ribosyldimethylarsine, require prolonged heating to be converted to reducible arsenic compounds [182]. Decomposition of arsenocholine and arsenobetaine by means of thermohydride generation [169,183] or UV photooxidation [159,184,185] has been reported.

The speciation analysis of organoarsenic species by LC with element-specific detection up to 1987 has been reviewed [186]. Anion-exchange

chromatography using an amine-bonded silica stationary phase is a simple and convenient method for simultaneous separation of As(III), As(V), MMA and DMA as well as phenylarsonic acid and triphenylarsine oxide. Ion-exchange and ion-interaction chromatography have been compared for the separation of As(III), As(V), MMA, DMA and arsenobetaine [164]. Anion pairing was found generally to be more sensitive to changes in the matrix of the sample injected. Anion exchange was more tolerant because of the higher buffering capacity of the mobile phase. Cation pairing was found to be suitable for the determination of DMA and arsenobetaine in salt-rich biological samples. The two inorganic forms of As were eluted with MMA but DMA and arsenobetaine were separated [164–166]. Cation exchange was found to be suitable for the separation of arsenobetaine and arsenocholine [141,145]. *Post-column* hydride generation for plasma spectrometry [149,152] and AAS [141,146,152,154] has been reported. Use of CZE for speciation analysis of As has been discussed but no application was reported [170].

Sample preparation usually involves homogenization and soaking of marine tissues with methanol [126,160] or HCl [187] or urine cleanup on a disposable C₁₈ cartridge [142]. Trypsin enzymolysis digestion of animal tissue has been reported [167].

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Barium

Barium (Ba, atomic weight 137.34, melting point 725°C, $d = 3.51 \text{ g cm}^{-3}$) is a silvery-white, soft metal. It occurs in the earth crust with the average abundance of 0.04%, primarily in barite (BaSO_4). Barium reacts with water; in solution it occurs entirely as Ba^{2+} . Barium hydroxide is a strong base fairly soluble in water. Barium chromate and sulphate are the least soluble of the corresponding alkaline earth metals. Barium does not form stable complexes. The water-soluble salts are poisonous. The demand for the trace analysis for Ba usually comes from the field of ecotoxicology and clinical toxicology.

16.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Barium can be separated from Sr by precipitating BaSO_4 in the presence of EDTA (pH 8) or BaCrO_4 in the presence of DCTA (pH 6–7). Chromatographic methods include cation exchange [1] and extraction chromatography using the 18-crown-6 coated silica as stationary phase [2,3]. The practical significance of extraction is restricted to the separation of Ba complexes with dibenzo-18-crown-6 in the presence of picrate [4] or TTA [5].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.5 \text{ } \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame at the most sensitive 553.6 nm line. Ionization should be controlled by the addition of an alkali metal salt (e.g. KCl) to samples and standards. In the presence of Ca, absorption from the CaOH band occurs at the 553.6 nm line which makes background correction necessary [6]. The effects of Ca and Sr are reduced in the presence of Mg that is commonly added as a matrix modifier [6]. Interference of Al has been systematically investigated [7,8]; 8-hydroxyquinoline as pro-

tecting agent and La as releasing agent were recommended to suppress the Al interference in the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame. The use of an air- C_2H_2 flame was not efficient, even in the presence of La [7].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 6 pg (DL of 40 ng ml^{-1}) using the atomization from a pyrolytically coated tube wall. The determination is adversely affected by the low atomization efficiency (<10%) and the formation of thermally stable carbides, such as e.g. BaC_2^+ [9]. The refractory character of Ba and the high atomization temperature required preclude the use of a platform and reduce the tube lifetime, particularly in the presence of corrosive matrices [1,10,11]. Further, at the high atomization temperatures, graphite and matrix emit intense continuum radiation in the visible range which renders efficient D_2 background correction impossible. The Zeeman correction is required unless a second continuum source such as a tungsten halogen lamp is used. Ionization of Ba at temperatures higher than 2300°C can be significant which makes the addition of an easily ionizable element salt (e.g. KCl) necessary. The quality of the pyrolytic coating of a graphite tube was shown to be of primary importance [12,13]. The atomization efficiency can be improved by impregnating pyrocoated graphite tubes with Th, La, Ti, Mo, W and Y [9,10,14]. Alternatively, Ta- or W-coated platforms have been suggested [15–17]. Various electrothermal atomizers have been compared; a tungsten coil atomizer was recommended [18]. Molybdate, vanadate and molybdovanadate were used as releasing agents for Ba in the phosphate and silicate matrix [19]. Use of a V_2O_5 -Si matrix modifier was reported to prevent the formation of barium carbide [13]. Attempts to use a $\text{Pd-Mg}(\text{NO}_3)_2$ modifier were unsuccessful [10].

Atomic emission spectrometry

Barium gives an intense emission in an $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame at 553.6 nm which is the basis of its determination [5,20]. Magnesium was recommended as a matrix modifier [20]. Inductively coupled plasma AES offers a DL of 0.5 ng ml^{-1} at the most sensitive 455.4 and 493.53 nm lines which are apparently free of spectral overlaps [21–23]. Magnesium was found to be an effective excitation buffer in DCP AES that eliminated the effects of up to 4 mg ml^{-1} of both Ca and Sr [6].

Mass spectrometry

Barium has seven naturally occurring isotopes: ^{130}Ba (0.1%), ^{132}Ba (0.1%), ^{134}Ba (2.42%), ^{135}Ba (6.59%), ^{136}Ba (7.85%), ^{137}Ba (11.23%) and

^{138}Ba (71.7%). Thermal ionization MS is seriously hampered by contamination. Inductively coupled plasma MS offers a DL of 0.03 ng ml^{-1} [24]. A combination of low abundances and isobaric interferences from Xe (an impurity in argon gas) precludes the use of ^{130}Ba , ^{132}Ba , ^{134}Ba and ^{136}Ba ions [24]. In addition, ^{138}Ba is overlapped by ^{138}La and ^{138}Ce . Isotope dilution ICP MS determination using a ^{135}Ba spike has been developed [25].

Neutron activation analysis

This is usually based on the reaction $^{130}\text{Ba}(n,\gamma)^{131}\text{Ba}$ and counting the long-lived ^{131}Ba ($t_{1/2} = 13 \text{ d}$, many γ -lines). It is not particularly sensitive because of the low isotopic abundance of the ^{130}Ba . The short-lived ^{139}Ba ($t_{1/2} = 85 \text{ min}$, $E_{\gamma} = 0.163 \text{ MeV}$) can be used alternatively.

Other determination techniques

Barium gives sensitive colour reactions with several bisazo derivatives of chromotropic acid (especially Sulphonazo III) which, however, lack the necessary selectivity to be widely used in practice. The atomic spectrochemical determination of Ba is affected by the high and varying thermal stabilities of Ba compounds formed in the atomizer [19]. X-ray fluorescence is hampered by the spectral interference from Fe and fairly low sensitivity (DL $\sim 25 \text{ } \mu\text{g g}^{-1}$) [26].

16.2 ANALYSIS OF REAL SAMPLES

In environmental waters the Ba level ranges from $1 \text{ } \mu\text{g l}^{-1}$ in surface waters to hundreds of $\mu\text{g l}^{-1}$ in anoxic, organic-rich sedimentary pore waters [25]. Barium shows lowest concentrations near the surface and enrichment at depth [13]. Many samples can be analyzed directly by GF AAS [10,12,13]. Pyrolysis at 1800°C eliminates the non-specific absorption of the matrix [12]. Problems encountered in the direct determination of Ba by GF AAS in seawater have been comprehensively discussed [13]. An alternative is direct ICP AES [22,23] or, better, ICP MS that is able to cope even with highly dilute samples [24,25]. Barium concentrations in solutions of biological materials digests are in the range $0.01\text{--}1 \text{ } \mu\text{g ml}^{-1}$ and are readily determined by ICP AES [21] or GF AAS [6]. An intercavity laser spectroscopic method was reported to achieve a DL of 0.2 ng l^{-1} after ETV [27].

Preliminary separation of Ba by ion exchange [1] or extraction [28] bears a severe contamination risk. Commercial cation exchangers were reported to contain up to $1 \text{ } \mu\text{g g}^{-1}$ of Ba which can be removed down to

0.04 $\mu\text{g g}^{-1}$ by rinsing and conversion to the NH_4^+ form [1]. Barium is difficult to exclude from the distilled reagents used for column elutions [25]. Severe contamination problems were reported from polyethylene sampling cups [10].

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Beryllium

Beryllium (Be, atomic weight 9.01, melting point 1287°C, $d = 1.85 \text{ g cm}^{-3}$) is a grey, hard metal. Beryllium is largely dispersed in the earth's crust with an average abundance of 2–3.5 ppm. The metal dissolves readily in dilute H_2SO_4 and dilute or concentrated HCl but it is passivated by concentrated HNO_3 . Beryllium dissolves in alkalis to form beryllate, $\text{Be}(\text{OH})_4^{2-}$, with the evolution of H_2 . Beryllium occurs at the II oxidation state; in aqueous media it is present as Be^{2+} , $\text{Be}(\text{OH})_4^{2-}$, or various polymeric hydroxospecies. The hydroxide, $\text{Be}(\text{OH})_2$, which precipitates at pH 6 dissolves in alkalis (but not in $\text{NH}_3(\text{aq})$). Beryllium salts are water soluble except for molybdate and phosphate. Beryllium forms strong complexes with fluoride (BeF_4^{2-}), chloride and with *O*-donor ligands. Trace analysis for Be is demanded in atmospheric chemistry (^7Be , ^9Be and ^{10}Be are produced in the upper atmosphere), geochemistry (tracing of magma crystallization processes), industrial quality control (Be is used to improve mechanical and corrosion resistance of alloys) and occupational hygiene (Be and its compounds are highly toxic).

17.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Beryllium can be fairly selectively extracted as the complex with acetylacetone in the pH range 4–9 into CCl_4 , MIBK or benzene [1–4]. EDTA is added to mask foreign ions [1–3,5]. Beryllium can be stripped into HNO_3 [2,3]. Other extraction systems included a β -diketo liquid exchanger (cyclohexane) [6] and BPHA (MIBK) [7]. Coprecipitation of Be with $\text{Hf}(\text{OH})_4$ [8] and $\text{Sn}(\text{OH})_4$ [9] has been reported. Less common

preconcentration methods include selective retention of Be on the outer wall of *Escherichia coli* at pH 6–9 [10] or sorption of Be complexes with CAS or acetylacetone on polyethylene powder [11] or activated carbon [5], respectively.

Spectrophotometry and spectrofluorometry

Most methods are based on ternary systems involving a triphenyl-methane dye (e.g. Chrome Azurol S or Eriochrome Cyanine R) and a cationic surfactant (CTA, CP or Zephiramine). The methods are sensitive ($\varepsilon \approx 1 \times 10^5$) whereas selectivity is considerably improved in the presence of EDTA. Spectrofluorimetric reagents include morin [11,12] and Nuclear Fast Red [4]. A variety of interferences which can be apparently alleviated by optimization of reaction conditions and masking make these methods unreliable and time consuming in the case of more complex matrices.

Flame atomic absorption spectrometry

An $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame is recommended to give a sensitivity of $0.025 \mu\text{g ml}^{-1}$ at the most sensitive 234.9 nm line. High concentrations of Al, Si and Mg depress the Be signal. The Al-interference has been systematically studied [7]. It can be controlled (up to 1 g l^{-1}) by the addition of HF [13] or La, EDTA and 8-hydroxyquinoline [14] but at higher concentrations a chemical separation must be applied. The interfering effects of Si and Mg were alleviated by adding 8-hydroxyquinoline [14].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass 0.5 pg (DL 8 pg ml^{-1}) when pyrolytically coated tubes and platform atomization are used. Nitrates of La, Ca, Al, Mg and Sr can be used as modifiers [15]; the most common is $\text{Mg}(\text{NO}_3)_2$ [16–19]. The use of $\text{Al}(\text{NO}_3)_3$ is particularly recommended if HF is present, since it prevents the formation of the volatile BeF_2 by formation of the thermally stable Al_2BeO_4 [15]. The modifier can be avoided by using atomization from the L'vov platform treated with $\text{Th}(\text{NO}_3)_4$ [16]. Zirconium-coated tubes have been used to remove Al interference [3]. Slurry GF AAS of charcoal [5], coal [20] or biosorbents [10] has been reported. The possibility of standardless determination of Be in environmental and biological samples with Pd matrix modification has been discussed [21].

TABLE 17.1

Methods for the determination of beryllium in water

Water (amount)	Separation and/or preconcentration	Detection technique	DL (ng/l)	Ref.
Sea (0.2 l), rain (0.1 l)	sorption of the acetylacetonate complex on activated carbon	GF AAS	1 ^a	5
Tap	sorption of Chrome Azurol S complex on polyethylene powder	GF AAS	800	11
Tap	anion exchange	FLU	200	11
Lake (0.03 l)	extraction with acetylacetone (CHCl ₃), GC	MIP AES	0.3	22
Tap, natural (1 l)	anion exchange	solid phase VIS	6	23

^a Absolute detection limit, pg.*Atomic emission spectrometry*

Emission in an N₂O–C₂H₂ flame is preferably measured at 234.9 nm. ICP AES offers DLs of 0.1–0.5 ng ml⁻¹ at 234.86, 313.04 and 313.11 nm. The determination at the 313.042 nm is interfered with by V (313.027 nm) and Ti (313.080 nm), and OH bands and it is recommended that it be preceded by separation of Be.

17.2 ANALYSIS OF REAL SAMPLES

Beryllium is determined in various samples in a multielement array, often directly after sample decomposition (*cf.* Part II). Methods developed for Be solely are summarized in Table 17.1 (water) and Table 17.2 (geochemical and biological materials).

Environmental samples

Those with Be concentrations above 1 µg g⁻¹ are preferably analyzed by GF AAS using Mg(NO₃)₂ matrix modifier, D₂ background correction and calibration by standard additions [8]. Use of Al(NO₃)₃ as a modifier was

TABLE 17.2

Methods for the determination of Be in environmental and biological samples

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection technique	DL ($\mu\text{g/g}$)	Ref.
CRMs	none	retention on <i>Escherichia coli</i> (pH 6–9)	GF AAS	0.05 ^b	10
Soil (2 g)	HF–HNO ₃ – HClO ₄	extraction as acetylacetonate (benzene), back- extrn. (HNO ₃)	GF AAS	1.5 ^b	3
Soil, coal, ashes (0.1 g)	XeF ₄ (bomb)	extraction as trifluoroacetyl- acetate (CS ₂ , benzene), selective vaporization	ICP AFS	0.0005 ^b	24
Fly ash (0.5 g)	fusion with LiBO ₂ , dissolution in HNO ₃	none	GF AAS	0.09	18
Fly ash	HF, HCl–HNO ₃	extraction with C ₉ H ₁₉ COCH ₂ – COCH ₂ (cyclo- hexane)	GF AAS	n.g.	6
Fly ash, CRM sediments, coal (0.5 g)	HNO ₃ , HF–HClO ₄	none	GF AAS	0.03 ^b	16
Sediments (0.025–0.1 g)	HF–HNO ₃ (microwave assisted)	none	GF AAS	1.6 ^a	15
Sediment CRMs plant (0.2 g)	dry ashing, HNO ₃ , HClO ₄ , HF	cation exchange, anion exchange	GF AAS	0.5 ^b	25
Plants (5 g)	HNO ₃ –H ₂ O ₂	extraction as acetylacetonate (MIBK), back- extrn. (HNO ₃)	GF AAS	1.5 ^b	2

^a Absolute detection limit, pg; ^b In the solution fed, ng/ml.

recommended for fluoride-containing sample digests [15] whereas $\text{Mg}(\text{NO}_3)_2$ was preferred after metaborate fusion [18]. For Be contents below $1 \mu\text{g g}^{-1}$ the modifier's blank is too high so the modifier must be avoided [16]. Sequential leaching has been used for the determination of fractionation of the stable (^9Be) and the cosmogenic (^{10}Be) beryllium isotopes [26]. Efficient preconcentration, e.g. by sorption, is required to match the concentrations of Be in natural waters for analysis by GF AAS [5].

Biological materials

Beryllium in clinical samples is determined directly by GF AAS using $\text{Mg}(\text{NO}_3)_2$ as matrix modifier [17,19]. A detection limit down to 0.05 ng ml^{-1} can be achieved. Zeeman correction was indispensable for eliminating non-specific absorption; D_2 correction gave equivalent results provided that samples were diluted at least five times [19]. A mixture of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ and ascorbic acid was employed as a matrix modifier for the determination of Be in urine (D_2 background correction) [27].

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Bismuth

Bismuth (atomic weight 208.98, melting point 271°C, $d = 9.75 \text{ g cm}^{-3}$) is a greyish-white lustrous metal, produced as a by-product in the refining of Pb, Cu, Sn and Au ores. The average earth's crust abundance of Bi is 0.2 ppm. Bismuth is inert to dilute non-oxidizing acids but it dissolves readily in HNO_3 . It occurs in the -III, III and V valence states, the III being the most common. Bismuth(III) hydrolyzes at pH 1–2 and shows no amphoteric properties. Bismuth(III) forms citrate, oxalate, iodide, thiosulphate, and EDTA complexes. Bismuth(V) is a strong oxidant. Trace analysis for Bi is demanded in geochemical studies, industrial quality control and medicine (monitoring for Bi drugs).

18.1 SEPARATION AND PRECONCENTRATION

Volatilization

The Bi hydride (BiH_3 , bismuthine) is produced in acid medium, usually 1 M HCl by reduction of Bi(III) by NaBH_4 [1]. Since it is fairly unstable and decomposes on heating upon the cryogenic trapping, it is preferably trapped in a graphite tube [2]. The BiH_3 generation is severely interfered with by Ni, Cu, Co which may form intermetallic compounds with Bi [3,4]. Selenium may precipitate. Arsenic, Sb and Sn compete for the reagent to form hydrides [4]. The interferences are usually alleviated by masking with ascorbic acid, iodide and thiourea [1,5] or ion-exchange separation [6]. Copper matrix can be removed by electrolysis [4] or masked with thiosemicarbazide [7]. 1,10-Phenanthroline has been used to minimize the Ni interference [8].

Extraction

Bismuth is efficiently extracted with dithizone or DDTC. High selectivity is achieved by using Pb-DDTC as extractant [9]. Bismuth iodide was extracted into MIBK and then Bi was stripped into an aqueous EDTA solution [10]. Bismuth was extracted with high molecular amines or quaternary salt from halide media into nonpolar solvents [11,12].

Precipitation

Precipitation of Bi as hydroxide or sulphide in the presence of suitable collectors is possible but seldom used because of the lack of selectivity [13].

Sorption

Sorption of Bi on thioanilide-loaded silica [14] or as a complex with 2-mercaptobenzothiazole [15] or xanthate [16] on microcrystalline naphthalene [15] or activated carbon [16] was reported. Bismuth can be separated on cation exchangers [17–19] or anion exchangers (as Tiron or Pyrocatechol Violet complex) [20], or on chelating resins [21].

18.2 DETERMINATION TECHNIQUES

Spectrophotometry

Dithizone forms an orange-brown dithizonate which is extracted into CHCl_3 or CCl_4 and is stable over the pH range 3–9.5. The method is fairly sensitive ($\epsilon = 7.9 \times 10^4$ at 490 nm) and selective in the presence of cyanide and tartrate. The interfering Pb and Tl(I) can be stripped at pH 3.3. Extraction-spectrophotometric determination of Bi with Pb-DDTC was reported in the FI mode [9].

Flame atomic absorption spectrometry

A sensitivity of $0.2\text{--}0.5 \mu\text{g ml}^{-1}$ is obtained in the recommended air- C_2H_2 oxidizing flame (lean, blue) at the most sensitive 223.1 nm line (actually a doublet at 222.8 and 223.1 nm). A silica collection tube has been proposed to increase the sensitivity [22]. An EDL is available but no gain in sensitivity is apparently achieved.

Quartz furnace atomic absorption spectrometry

Quartz furnace AAS with an electrothermally heated cell offers a detection limit of *ca* 0.02 ng ml^{-1} and is easily automated [3,5,23]. Bismuth is introduced as the hydride.

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 20–30 pg (ADL of 1–2 pg). Low-temperature atomization is favoured due to the volatility of Bi [24], in particular as chloride [25]. A matrix modifier is essential to prevent Bi volatilization prior to atomization. Nickel [26], Pt [27] or the mixtures: $\text{Pd}(\text{NO}_3)_2\text{--Mg}(\text{NO}_3)_2$ [28], $\text{PdCl}_2\text{--NH}_4\text{NO}_3$ [29], $\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4\text{--Na}_3\text{PO}_4$ [24], $\text{Ni}(\text{NO}_3)_2\text{--Cu}(\text{NO}_3)_2$ [30], $\text{NH}_4\text{--EDTA--Ni}(\text{NO}_3)_2\text{--Cu}(\text{NO}_3)_2$ [31] have been proposed. The chloride interference can be removed by masking Bi with EDTA preventing the formation of chloride [25,30]. The enhancing effects on the absorbance of Bi caused by Al and Fe(II) was minimized by the addition of aluminium to both samples and calibration standards [5]. Atomization is promoted by the addition of 10% H_2 in the Ar sheath gas [24]. The high non-specific absorption encountered in the determination of Bi in nickel-base alloys with D_2 background correction could not be eliminated by chemical modifiers; a separation step was necessary [13].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers DL of 30–70 ng ml⁻¹ at the 223.06, 306.77 and 222.83 nm lines. Spectral overlap of Cu occurs at the 223.06 and 222.83 nm lines. The latter line is also interfered by Fe. The sensitivity and selectivity are greatly improved by introducing Bi as BiH_3 [1]. Bismuthine generation in the presence of KI and either $\text{K}_2\text{Cr}_2\text{O}_7$ or H_2O_2 is particularly suitable as the liberated I_2 enhances the atomization and/or excitation of Bi atoms in the ICP [1].

Neutron activation analysis

The (n, γ) reaction of Bi leads to ^{210}Pb ($t_{1/2} = 5.01$ d) which decays to its daughter ^{210}Po ($t_{1/2} = 138.4$ d). The β -emission of the latter is usually measured but a selective separation is necessary.

Other techniques

Bismuth has only one stable nuclide ^{209}Bi which is used for ICP MS [11,32,33]. Non-dispersive AFS using atomization in an Ar- H_2 flame offers a detection limit of 30 pg and excellent reproducibility [34].

18.3 ANALYSIS OF REAL SAMPLES

Methods for the determination of trace Bi amounts are summarized in Tables 18.1–18.4 for water, geological, biological and industrial

TABLE 18.1

Determination of bismuth in water

Water (amount)	Separation and/or preconcentration	Detection technique	Detection limit (ng/l)	Ref.
Waste	volatilization as BiH_3	ICP AES	350	1
Sea (1 l)	extraction with <i>i</i> -TOA (heptane), back-extraction (conc. HNO_3)	ICP MS	3	11
Sea (1 l)	copptn. as $\text{Bi}(\text{OH})_3$, volatn. as BiH_3 , trapping in a GF	GF AAS	3 ^a	2
River (1.5 l)	sorption on thionalide-loaded silica, volatilization as BiH_3	QF AAS	1	35
Rain, river, lake	sorption on thioanilide-loaded silica, elution with 4 M HCl, volatilization as BiH_3	AAS	1 ^a	14

^a Absolute detection limit, ng.

samples respectively. Hydride generation following a classical sample decomposition procedure is the most common approach. Quartz furnace AAS, ICP AES and ICP MS are the usual techniques of choice.

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TABLE 18.2

Determination of bismuth in geological materials

Sample (amount)	Dissolution	Separation and/or preconcentration	Detection technique	DL (μg/g)	Ref.
CRMs (0.5 g)	<i>aqua regia</i> (bomb)	volatilization as BiH ₃	FI AFS	30 ^a	34
CRMs (0.2–1 g)	HF–HClO ₄ –HNO ₃	extraction as BiI ₄ (MIBK), stripping with EDTA	FAAS	0.4	10
CRM rocks (1 g)	HF–HClO ₄	volatilization as BiH ₃	ICP MS	0.07	36
CRM rocks, sediments (0.1–0.5 g)	HNO ₃ –HF–HClO ₄	sorption of xanthogenate complex on activated carbon	GF AAS	0.05 ^b	16
CRMs (0.3–0.5 g)	HCl–HNO ₃ –HF or H ₂ O ₂ –HNO ₃ –HF–H ₂ SO ₄	extraction with TOMA (xylene)	GF AAS		12
CRM sediments (0.2 g)	HNO ₃ –HClO ₄ –HF	none	GF AAS	n.g.	24
CRM fly ash, rocks, ores (0.5–1 g)	HClO ₄ –HNO ₃ –HF	volatilization as BiH ₃	QF AAS	0.005	5
CRM fly ash (0.5 g), CRM ores, clays (0.5–1 g)	HNO ₃ –HCl; HClO ₄ –HNO ₃ –HF	volatilization as BiH ₃	ICP AES	0.35 ^b	1
Ores (0.5 g)	HNO ₃ –HClO ₄	cation exchange	VIS	n.g.	21
Sediment (0.5 g)	HNO ₃ , HClO ₄ , HCl–HF	volatilization as BiH ₃ , trapping in a GF	GF AAS	3	2
Atmospheric particulates	H ₂ SO ₄ –H ₂ O ₂ –HF	volatilization as BiH ₃	AAS	0.08 ^c	37
Soil (10 g)	<i>aqua regia</i> (leaching)	sorption on activated carbon as APDC complex	QF AAS	n.g.	22

^a Absolute detection limit, pg; ^b in the solution fed, ng/ml; ^c in the sample, ng/m³.

TABLE 18.3

Determination of bismuth in biological materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection technique	DL (ng)	Ref.
Urine, serum, plasma, bile juice	HNO ₃	volatilization as BiH ₃	FAAS	n.g.	38
Serum (1 ml), urine	HNO ₃	none	GF AAS	n.g.	29
Plasma, urine, erythrocytes	HNO ₃	volatilization as BiH ₃	QF AAS	n.g.	39
Liver, kidney, brain, mucosa (0.5–2 g)	HNO ₃ , HCl	volatilization as BiH ₃	QF AAS	n.g.	38
CRM plant (0.5 g)	H ₂ SO ₄ –H ₂ O ₂	volatilization as BiH ₃	QF AAS	3	37
Algae (0.5 g), shells (5 g)	HNO ₃ , HClO ₄ , HCl–HF	volatilization as BiH ₃ , trapping in a GF	GF AAS	0.003	2

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TABLE 18.4

Determination of bismuth in industrial materials

Sample (amount)	Dissolution	Separation and/or preconcentration	Detection technique	DL ($\mu\text{g/g}$)	Ref.
Copper (0.5 g)	HNO_3	volatilization as BiH_3	ICP AES	0.35 ^b	1
Copper (0.2 g)	HNO_3	masking Cu with thiosemicarbazide	FAAS	1	7
Copper, silver, Ag-Cu alloys (1 g)	HNO_3	cation exchange, volatilization as BiH_3	AAS	n.g.	21
CRM copper (0.5 g)	HNO_3	electrolytic removal of Cu, volatilization as BiH_3	FAAS	70 ^a	4
CRM copper, lead	HNO_3	adsorption on a TOPO-modified tungsten wire	GF AAS	n.g.	40
Aluminium	$\text{HCl-H}_2\text{O}_2$	none	GF AAS	n.g.	30
Al-based alloys	n.g.	sorption of 2- mercaptobenzo- thiazole complex on microcrystalline naphthalene	FAAS	n.g.	15
CRM Al-based alloys (0.5 g)	HCl	volatilization as BiH_3	ICP AES	0.35 ^b	1
CRM steel, alloys, lead gun metal	n.g.	volatilization as BiH_3	QF AAS	0.2 ^a	3
CRM steels (0.1 g)	HCl-HNO_3	volatilization as BiH_3	ICP AES	1	41
Thallium reagents	HNO_3	cation exchange	GF AAS	0.1	18
Zn, Pb, Cu concentrates (0.5 g)	$\text{HClO}_4\text{-HNO}_3$	cation exchange	VIS	n.g.	21

^a Absolute detection limit, ng; ^b in the solution fed, ng/ml.

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Boron

Boron (B, atomic weight 10.81, $d = 2.34 \text{ g cm}^{-3}$) is a metalloid that exists as a brown amorphous powder or, in higher purity, as dark grey crystals. Boron occurs in the earth's crust with an average abundance of 0.001%, principally in colemanites. Boron is widely used in electronics as dopant of amorphous silicon. Boron (^{10}B) is an effective neutron absorber in the nuclear industry and is used as a hardener for steel and high purity metals. Boron is an essential micronutrient for plants but is toxic at higher concentrations. In medicine boron compounds are used in cancer therapy. Boron is a valuable tracer of various geochemical processes and of industrial pollution.

Boron is unattacked by non-oxidizing acids and hot concentrated alkalis but readily dissolves in concentrated HNO_3 and oxidizing mixtures. On fusion with alkali metal hydroxides, carbonates or peroxides, boron is oxidized to borate. Most metal borates, apart from those of alkali metals, NH_4^+ and Tl(I) , are sparingly soluble in water but dissolve in acidic solutions. In analytical chemistry only B(III) compounds are of importance. In water a number of oxy-anions are present: orthoborate (BO_3^{3-}), metaborate (BO_2^-) and tetraborate ($\text{B}_4\text{O}_7^{2-}$) which are related to each other by hydration-dehydration reactions. In aqueous solution, boric acid reacts with HCl and HF to produce volatile boron fluoride (BF_3) and chloride (BCl_3), respectively. In excess of HF involatile tetrafluoroboric acid (HBF_4) is formed. In anhydrous medium, boric acid reacts with methanol to form volatile trimethyl borate. Several boron hydrides (boranes) are also known. Boric acid and metal borates are toxic in large amounts whereas the boron hydrides are very poisonous.

19.1 SEPARATION AND PRECONCENTRATION

Volatilization

Volatilization of low boiling boron compounds: borofluoride (boiling point -101°C), trimethyl borate (boiling point 69°C) or diborane, B_2H_6 (boiling point -92.5°C) is widely used for the separation of B from the sample matrix [1–9]. Boron fluoride, BF_3 , is usually distilled from an HF medium in the presence of H_2SO_4 using a N_2 carrier stream in a Teflon apparatus. The generation of trimethyl borate is an esterification reaction which requires an addition of concentrated H_2SO_4 and methanol. The heat to volatilize the trimethyl borate can be produced either by the addition of a small volume of water to the H_2SO_4 solution or by heating the aqueous phase in a water bath prior to methanol injection. The inhibiting effect of water which is also a reaction product of the esterification can be eliminated by the addition of saturated $\text{Ca}(\text{OH})_2$ to the sample and its evaporation prior to distillation of the trimethyl borate [5]. The interference of fluoride which masks the boron can be removed by adding Al^{3+} which leads to the formation of AlF_4^- instead of BF_4^- [5]. The distilled trimethyl borate can be sorbed in a 4% NaOH solution [4,7] or water [2,5], or conveyed in a carrier stream directly to the atomizer [1,3,6]. An intermediate condensation step is often incorporated to increase the sensitivity. Diborane generation by heating a solid mixture of borate and LiAlH_4 at 160°C has been reported [9].

Extraction

Boron can be separated by extraction of H_3BO_3 with 1,3-diols, typically with 2-methylpentane-2,4-diol or 2-ethylhexane-1,3-diol [10,11]. Extraction of ion associates of BF_4^- with onium cations or basic dyes (e.g. Methylene Blue) has been used [12].

Ion exchange

Cation exchangers [7,13–16] or chelating resins, e.g. Chelex-100 [14], do not retain B while removing dissolved cations. They are recommended to be used prior to sensitive determination techniques with low tolerance to the dissolved salts, e.g. ICP–MS. Conversely, anion exchangers which retain boron selectively are preferred in the analysis of samples with low boron concentration or when poorly sensitive techniques are used. Synthetic boron-binding resins (Amberlite XE-243, Amberlite IRA 743) contain a hydrophobic styrene backbone and N-methylglucamine groups. The latter complex borate ions while matrix

components are eluted with $\text{NH}_3(\text{aq})$. Boron can be eluted with HCl [17–20] or 1% HNO_3 [21]. A more complex scheme is based on the conversion of the borate into BF_4^- (with 10% HF), which is quantitatively retained on the tertiary amine groups and subsequently eluted with NaOH [14]. Another possibility is anion exchange of the boron–mannitol complex [22].

19.2 DETERMINATION TECHNIQUES

The position of spectrophotometry, although considerably recently eroded by ICP–AES because of often insufficient sensitivity and interferences, is remarkably strong. This is due to many difficulties occurring in AAS (formation of a thermally stable carbide), XRF (low atomic weight) and NAA (the lack of a suitable nuclear reaction).

Spectrophotometry

In acid non-aqueous media, curcumin and boron form a violet–red complex called rosocyanin. The curcumin method offers an exceptionally high sensitivity ($\epsilon = 1.8 \times 10^5$ at 550 nm) but results depend critically on the quality of the reagent. Numerous elements, oxidants and anions (fluoride) interfere so a separation step is mandatory. Other common reagents include Carmine (Carmine Red, a glycoside derivative of the α -hydroxyanthraquinone) [10,11,19] and Azomethine-H [5,19,23–27] both requiring separation of B prior to determination. An alternative is the extraction of an ion pair of BF_4^- with Methylene Blue [12,28].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of about $10 \mu\text{g ml}^{-1}$ at the most sensitive 249.7 nm line in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$, reducing (rich, very red) flame. Atomization of trimethyl borate gas with a D_2 background correction is recommended. Fluoride interference can be overcome by adding Al^{3+} [29].

Electrothermal atomic absorption spectrometry

The determination of B by GF AAS is difficult because of the involatile nature of this element (boiling point 2550°C) and the formation of a refractory carbide (boiling point 3500°C). The latter reduces the tube lifetime and is responsible for the memory effect. The loss of sensitivity can be prevented by adding matrix modifiers usually alkaline earth

metals (as salts) which form with B more volatile species (e.g. calcium boride). The memory effects were removed by injecting NaF and a $\text{CH}_3\text{OH}-\text{H}_2\text{SO}_4$ mixture between measurements to destroy the residual boron carbide [30]. An alternative is the pretreatment of the graphite tube with a carbide-forming element (e.g. Zr). When combined with the use of a Ni modifier it was reported to give high sensitivity (80 pg), a negligible memory effect and an increased tube lifetime. The use of a Zr-treated L'vov platform gave lower sensitivity than that obtained with pyrolytically coated graphite tubes [30]. The latter, however, showed a considerably longer lifetime and allowed for the determination of B at high atomization temperatures on the routine basis. The memory effect was also eliminated [31]. Another difficulty is associated with loss of molecular boron forms below the appearance of atomic boron which cannot be prevented with the $\text{Ni}(\text{NO}_3)_2$ modifier [32]. Electrothermal AAS was applied to the indirect determination of boron after extraction of the ion pair of the Cd-1,10-phenanthroline cation with BF_4^- and measurement of the Cd signal [33].

Flame atomic emission spectrometry

Molecular emission of boron oxide at 518 nm or the BO_2 radical at 547.8 nm [34,35] is measured. Introduction of trimethyl borate or diborane vapour into an H_2 diffusion flame [9] is recommended to avoid interferences from alkali and alkaline earth elements. Fluoride greatly diminishes the flame [36] and plasma [37] emission of boron in methanolic solutions. This effect is caused by the replacement of a B–O bond by a B–F bond leading to the formation of the stable and involatile BF_4^- [34]. The presence of elements that form stable complexes with fluoride reduces the interference.

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers high sensitivity (a detection limit of 2–3 ng ml⁻¹) at the most sensitive lines: B I 249.773 nm and 249.678 nm [38,39]. Both lines are interfered with iron, because of the spectral overlap with Fe II at 249.772 nm and Fe I at 249.65 and 249.70 nm. The separation of B from the matrix or instrumental correction for the Fe content is required. The side line indexing method in scanning ICP AES was used to overcome the Fe interference in the determination of B in soils [40]. The iron interference free lines (B I at 208.959 nm and B I 208.893 nm) are less sensitive and are often not suitable to be used for the analysis at lower levels. The choice of wavelength is of particular

importance in the determination of B in refractory metals because of a high density of their emission lines in the spectral range used for B measurements. The 249.678-nm line was chosen for B determination in tantalum and the 249.773-nm line in W, Mo, Co, Nb and Ti metals [39]. To avoid interferences volatilization of trimethyl borate is the usual approach [3,6]. Care must be taken to remove excess of methanol to prevent quenching of the plasma. A sensitivity enhancement (DL 0.1 ng ml⁻¹) and freedom from interferences were observed by ETV ICP AES using NaOH-(NH₄)₂HPO₄ as a matrix modifier [41]. With GF furnace volatilization addition of polytetrafluoroethylene to the sample prevents the formation of refractory carbide and eliminates the memory effects [42]. The filament vaporization has been proposed for the analysis of amorphous silicon [43,44].

Thermal ionization mass spectrometry

Boron has two naturally occurring isotopes ¹⁰B and ¹¹B with natural abundances of 19.78% and 80.22%, respectively. Thermal ionization MS of Na₂BO₂⁺ has been widely applied to the determination of B [17,18,45] and its isotope ratios [13,17]. The ion emission intensity is strongly dependent on the ratio of the NaOH and H₃BO₃ used to form the borax. The chemical stoichiometry problems are alleviated by thermal ionization of Cs₂BO₂⁺ after direct fusion of the sample with Cs₂CO₃ on a tantalum filament [2,22,46–48]. High concentrations of dissolved organic carbon suppress formation of Cs₂BO₂⁺ ions [2]. Chemical ionization MS has been proposed to quantitate the ¹⁰B isotope from the ¹¹B/¹⁰B ratio in enriched boron by using the (CH₃O)₃BH⁺ ion. Direct introduction of trimethyl borate into the ion source has been employed [1].

Inductively coupled plasma mass spectrometry

Inductively coupled plasma MS offers high sensitivity (ca. 0.4 ng ml⁻¹) and selectivity [7,14,49]. A serious concern is the matrix-induced mass discrimination which can be significant owing to the proportionally large mass difference between ¹⁰B and ¹¹B [14]. Consequently an apparent increase in the measured ¹⁰B/¹¹B ratio in the presence of an abundant matrix component such as Na, is observed [14]. Therefore, a separation of B from the matrix is advised. The intense peak from ¹²C⁺ in biological samples can complicate the measurement of ¹¹B⁺ so it is advisable to use ¹⁰B instead [50,51]. The ¹¹B⁺ can be resolved from carbon in HR mode [24,50]. Use of ETV ICP MS with a Ni matrix modifier has been reported [32].

19.3 ANALYSIS OF REAL SAMPLES

General

Boron standard solution is prepared on the basis of H_3BO_3 and must be stored in a polyethylene bottle. If standard glassware is used, HF should be avoided since it attacks borosilicate glass leading to elevated blanks. The excess fluoride can be complexed with Al^{3+} to protect the borosilicate and quartzware and to release boron from the stable BF_4^- [52]. The use of a PTFE ware and sample introduction system for ICP is recommended [53]. Boron is often lost during decomposition or evaporation of HF containing solutions because of the high volatility of BF_3 [54]. Many workers added mannitol to prevent losses of B [22,33,52,55], but sometimes low recoveries were still observed. In some works H_3PO_4 was added to HF- HNO_3 [44] and HF- HNO_3 - HClO_4 [40] mixtures to prevent losses. Contamination from mineral acids and fluxes is common [21]. It is necessary to remove B from the reagents before use, e.g. by a boron-selective anion-exchange resin. Closed systems, made of an inert material and having a minimum surface area are recommended to reduce the risk of contamination and to minimize blanks.

Waters

Boron is found in natural waters, brines and pore fluids at concentration levels ranging from less than 1 pg l^{-1} to in excess of 200 mg l^{-1} depending on the nature and the source of the fluid. River and waste water samples were collected in polyethylene bottles, filtered and acidified with HNO_3 to $\text{pH} < 2$ [30]. Spectrophotometric methods for environmental waters were compared; the most sensitive Azomethine-H gave a DL down to $20 \text{ } \mu\text{g l}^{-1}$ [23]. Flow-injection sample introduction systems for water samples has been proposed [56]. Combined methods for the determination of B in waters are summarized in Table 19.1.

Geological materials

Colemanites are dissolved by refluxing with dilute HCl; this is best done in a quartz apparatus. *Aqua regia*, HNO_3 , HClO_4 are used to oxidize carbonaceous matter and dissolution of the silicate matrix is accomplished with HF [54]. Losses of boron occur on evaporating to dryness. Boron is often present in resistant minerals such as tourmaline for which fusion is favoured for sample decomposition. Fusion with Na_2CO_3 followed by the dissolution of the melt in dilute HCl or warm water is preferred. During this procedure the borate anion passes into

TABLE 19.1

Methods for the determination of boron in water

Water sample (amount)	Separation/ preconcentration	Detection	Detection limit (range)	Ref.
Fresh, saline (15 ml)	cation exchange	ID ICP MS	0.15 ^a	16
Fresh, saline (40 g)	anion exchange	VIS	(0.3–2) ^c	19
River, tap	anion exchange	ID TIMS	(5–250) ^a	17
Irrigation (5 ml)	volatn. as trimethyl borate	VIS	n.g.	5
Nuclear reactor (0.1 ml)	volatn. as trimethyl borate	FAES	0.15 ^d	34
Heavy water	volatn. with Cs ₂ CO ₃	TIMS	(0.04–17) ^b	46
Seawater	ion exchange	TIMS	n.g.	2

^a In ppb in the sample; ^b in ppm in the sample; ^c in ppm in the soln. analyzed; ^d absolute detection limit, μg .

an aqueous extract of the melt. Many of the rock constituents (Al, Fe, Ca) do not dissolve in the alkaline solution and must be removed by filtration or centrifugation. NaOH is less efficient and gives higher blanks [7]. The bulk of the flux can be easily removed by subsequent addition of HClO₄ [38]. Interference from Fe was eliminated by using Na₂CO₃–NaNO₃ fusion followed by an aqueous leach [57]. Boron can be separated from a carbonate melt by distillation of its methyl ester after acidification. Pyrohydrolytic leaching of B from rocks has been developed [2]. Boron is usually leached from soils with hot water [58] or CaCl₂ [26] solutions. The methods for the determination of B in geological materials are summarized in Table 19.2. Operational speciation of B in terms of total, leachable and mobile boron in sedimentary rocks has been discussed [20].

Biological samples

Serum can be analyzed on dilution with HCl by ICP AES with a DL of 0.7 ng ml⁻¹ [59]. Ashing or digestion of the sample is required to destroy the complex boron compounds (such as e.g. B₁₀H₁₀²⁻) prior to any combined procedure. Fusion with alkalis or sintering with Ba(OH)₂ or CaCO₃ [18] have been reported but losses of organically bound boron in the tissue are likely. The most common is tissue digestion with a H₂SO₄–H₂O₂ either open vessel [60] or with microwave-assisted high

TABLE 19.2

Methods for the determination of boron in geological samples

Sample (amount)	Decomposition	Separation	Detection	DL (range) ($\mu\text{g/g}$)	Ref.
Rocks (0.2 g)	fusion with K_2CO_3	none	ICP AES	2	38
Rocks (0.1–0.4 g)	fusion with Na_2CO_3	cation exchange	DCP AES	8 ^a	15
Rocks	fusion with K_2CO_3	anion exchange	VIS	n.g.	19
Rocks (0.5–1 g)	fusion with NaOH or Na_2CO_3	volatn. as trimethyl borate; removal of Na^+ by cation exchange	ICP MS		7
Rocks (0.15 g)	fusion with Na_2CO_3	extrn. with 2- ethylenehexane- 1,3-diol, stripping with NaOH	VIS	1	11
Rocks	leaching with HCl or fusion with Na_2CO_3	anion exchange preconcn., elimination of interferences by cation exchange	ICP MS		14
Sediments	fusion with Na_2CO_3	cation exchange	TIMS	n.g.	13
Soils (3 g)	HNO_3 , HF–HCl	<i>on-line</i> volatn. as trimethyl borate	ICP AES	50 ^a	6
Soils (0.2 g)	HNO_3 –HF– HClO_4 – H_3PO_4		ICP AES	n.g.	40
Soils, rock (1 g)	HF– <i>aqua regia</i>		ICP AES	5 ^a	54
CRMs	fusion with Na_2CO_3 – KNO_3	anion exchange	TIMS	(1–35)	17
CRMs (0.2 g)	fusion with Na_2CO_3 – NaNO_3		ICP AES	1	57
CRMs (1 g)	fusion with Na_2CO_3	extrn. with 2- ethylenehexane- 1,3-diol, stripping with NaOH	VIS	n.g.	10
CRMs	pyrohydrolysis	volatn. as trimethyl borate, conversion to $\text{Cs}_2\text{B}_4\text{O}_7$	TIMS	n.g.	2

^a In ng/ml in the solution analyzed.

pressure [24]. Care must be taken as this mixture reacts explosively with acetone [60]. Tumour samples were decomposed with concentrated HNO_3 in closed PTFE vessels [61]. Several determination methods of B in biotissues have been compared [24]. Measurement of ^{11}B by ICP MS is interfered with by the immense ^{12}C ; oxidation of the organic material with HNO_3 or HClO_4 is required often at the expense of higher blanks [50]. Procedures for the determination of B in biological materials are summarized in Table 19.3.

TABLE 19.3

Methods for the determination of boron in biological materials

Sample (amount)	Decomposition	Separation/preconcentration	Detection	DL (range) ($\mu\text{g/g}$)	Ref.
BioCRMs (0.5 g)	fusion with Na_2CO_3	anion exchange	ICP MS*	0.001	21
BioCRMs	$\text{Ba}(\text{OH})_2$	anion exchange	TIMS	(1–35)	17
Animal tissue (0.1–0.2 g)	$\text{HClO}_4\text{--H}_2\text{O}_2$	none	ICP AES	(0.05–100)	28
Animal tissue (0.05 g)	$\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$	none	DCP AES	0.1	60
Animal tissue (3–5 g)	$\text{HNO}_3\text{--H}_2\text{O}_2$	none	ICP AES	n.g.	62
Plant CRM (0.25–1.25 g)	$\text{Ba}(\text{OH})_2$ or CaCO_3	anion exchange	ID MS		18
Plant tissue (0.5 g)	$\text{HNO}_3\text{--HClO}_4$ (bomb)	volatn. as trimethyl borate	ICP AES	40 ^a	18
Plant tissue (0.4–0.5 g)	dry ashing	volatn. as trimethyl borate	FAAS	1.5 ^b	29
Plant tissue (5 g)	dry ashing, dissoln. in HCl		FI-VIS	n.g.	28
Plant CRM (0.2 g)	$\text{HNO}_3\text{--HF--HClO}_4\text{--H}_3\text{PO}_4$		ICP AES	n.g.	40
Wine (125 ml)	$\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$	volatn. as trimethyl borate	FAES	6 ^a	35

^a In ng/ml in the solution analyzed; ^b absolute detection limit, μg ; * $^{11}\text{B}/^{10}\text{B}$ isotope ratio measured.

Industrial samples

Metals, quartz and synthetic glasses are decomposed at a mildly elevated temperature in closed Teflon vessels. The oxidizing properties of the solvent are maintained by adding H_2O_2 to H_2SO_4 or HNO_3 . Methods for the determination of boron in industrial materials are summarized in Table 19.4.

TABLE 19.4

Methods for the determination of boron in industrial materials

Sample (amount)	Decomposition	Separation/pre-concentration	Detection technique	DL (range) ($\mu\text{g/g}$)	Ref.
Silicon	HNO_3 -HF	none	ETV ICP AES		44
Silicon (0.4 g)	HNO_3 -HF	matrix volatn. as SiF_4	DCP AES	0.8	44
Silicon (0.1 g)	HNO_3 -HF	extrn. as $\text{Cd}(\text{Ph})_3 \cdot 2\text{BF}_4$ (nitrobenzene)	indirect GF AAS	5 ^b	33
Silicon (0.1 g)	HF- HNO_3 , H_2SO_4	none	VIS	n.g.	63
Silica (0.4 g)	HF- HNO_3 -mannitol	matrix volatn. as SiF_4	DCP AES	0.8	55
Trichlorosilane (10 ml)	hydrolysis, dissoln. in HF	extrn. as $\text{Cd}(\text{Ph})_3 \cdot 2\text{BF}_4$ (nitrobenzene)	indirect GF AAS	5 ^b	33
Chlorosilane (10 ml)	hydrolysis, dissoln. in HF	none	VIS	n.g.	63
Steel (2 g)	n.g.	volatn. as trimethyl borate	ICP AES	20 ^b	8
Steels (1 g)	<i>aqua regia</i> , H_2SO_4 - H_3PO_4	volatn. as trimethyl borate	ICP AES	40 ^a	3
Iron, steel CRMs (0.5 g)	H_2SO_4 - H_3PO_4	volatn. as trimethyl borate	ICP AES	0.070	4

Sample (amount)	Decomposition	Separation/pre-concentration	Detection technique	DL (range) (µg/g)	Ref.
Titanium CRM	HF	none	ICP MS	1	64
Refractory metals	HF-HNO ₃ or H ₂ O ₂ (W)	none	ICP AES	from 0.4 (Ti) to 2.5 (Ta)	39
Coal (0.5 g)	HNO ₃ -HF	none	ICP AES	n.g.	65
Coal (1 g)	oxygen bomb, HF-HNO ₃	none	ICP AES	2	52
Fertilizers (CRMs)	HCl	anion exchange	ID TMS	(1-35)	17
Chemicals (100 ml)	none	extrn. as MB-BF ₄ into 1,2-dichloroethane	VIS	125 ^b	12

MB = Methylene Blue.

^a In ppb in the solution analyzed; ^b absolute detection limit, ng.

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Cadmium

Cadmium (Cd, atomic weight 112.4, melting point 321°C, $d = 8.64 \text{ g cm}^{-3}$) is a silvery white lustrous soft metal. It occurs in the earth's crust with an average abundance of 0.1 ppm, primarily in isomorphic forms with zinc in zinc blende (ZnS) or galmei (ZnCO₃). The metal dissolves readily in non-oxidizing acids (with evolution of H₂) and in HNO₃ (with formation of NH₄⁺ and evolution of N₂O). Cadmium exists in the II oxidation state; in aqueous solutions Cd²⁺ ions are present. Cadmium hydroxide is insoluble in excess of NaOH but dissolves in NH₃aq. Cadmium forms ammine, cyanide, halide and EDTA complexes. Cadmium sulphide (canary yellow) is precipitated by H₂S from dilute acids. The demand for trace determination of cadmium results primarily from its ecological and clinical toxicity.

20.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of the CdI₄²⁻ complex from iodide-H₂SO₄ solutions into oxygen-containing solvents (MIBK, mesityl oxide) is widely used [1]. The iodide [2] or chloride [3,4] complexes can be extracted with inert solvents as ion pairs with high molecular weight amines. Alternatively, Cd can be extracted with dithiocarbamates into MIBK [5,6] or inert solvents [7,8] and stripped with HNO₃ [8]. Dithizone allows a highly selective separation of Cd [9].

Sorption

Sorption on silica modified with 3-aminopropyltriethoxysilane [10,11], various chelating resins [12–15] or chelating agent loaded [16,17] resins

has been used. Alternatively, Cd chelates with PAN [18], DDTc [19] or APDC [20] have been sorbed on an inert support. Anion-exchange preconcentration as chloride complex has been reported [21]. Sorption is particularly convenient for application in *on-line* and FI systems [12,13,17,19,20].

Other methods

The utility of biological organisms for concentration of low trace Cd levels has been indicated [22,23]. Electrodeposition on Pt wire [24], W wire [25] and Hg-coated graphite platforms [26], and by *on-line* stripping voltammetry [27,28] has been proposed. Volatilization of Cd by its reaction with NaBH₄ [29] or with NaBEt₄ as well as in CF mode has been discussed [29–31]. The fairly unstable compound generated which was assumed to be the hydride, CdH₂, was stabilized with DMF or with didodecyldimethylammonium bromide vesicles [32]. Interferences from transition metal ions were attenuated by the use of citrate as a masking agent [30].

20.2 DETERMINATION TECHNIQUES

Spectrophotometry

The dithizone method based on the extraction of the pink dithizonate into CHCl₃ or CCl₄ from strongly alkaline media is sensitive ($\epsilon = 8.8 \times 10^4$ at 520 nm) and selective. The noble metals and Cu are removed beforehand by extraction with dithizone from acid media. Tartrate prevents the precipitation of hydroxides whereas Ni and Co are masked by dimethylglyoxime. The more sensitive method involving an azo reagent, 5-Br-PADAP, can also be recommended.

Flame atomic absorption spectrometry

Flame AAS using the air–C₂H₂ flame (oxidizing, blue) at the most sensitive 228.8 nm line is exceptionally sensitive and selective. Direct injection into flame from micro-sampling cups [33] offers a 10-fold increase in sensitivity. The effect of mineral acids on the cadmium FAAS signal has been studied [34]. High concentrations of silicate interfere. The determination of Cd levels below 50 ng ml⁻¹ in salt rich matrices requires extraction of a Cd halide into MIBK [1,2,5,6]. High volatility of Cd makes atom trapping in a silica tube mounted in the flame attractive to improve sensitivity down to 0.25 ng ml⁻¹ [35,36]. The effects of MgCl₂ and ascorbic acid on the volatilization of Cd have been studied

[37]. Lanthanum coating of the quartz tube has been proposed to prevent devitrification [38].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers high sensitivity (characteristic mass well below 1 pg) and good reproducibility. Pyrocoated graphite tubes or platforms are typically used. Because of the high volatility of Cd in a simple aqueous medium the pyrolysis temperature cannot exceed 380°C [39] and matrix modification is required. Typical modifiers have included HNO_3 [12,18,31] and $(\text{NH}_4)_2\text{HPO}_4$ [40–44]. Their mixtures proved to be more effective [9,45–48] but nevertheless losses of Cd can be expected at 600–700°C. Addition of Pd stabilized Cd to a similar extent as $\text{NH}_4\text{H}_2\text{PO}_4$ did but the increase in background signal associated with the latter was avoided [39,49,50]. Mixtures of Pd with $\text{Mg}(\text{NO}_3)_2$ [51–53], NH_4NO_3 [50,51,54] or ascorbic acid [55] were better suited. Oxalic, lactic, citric and ascorbic acids and EDTA were found to suppress interferences, oxalic acid was the only one not to produce a significant background [56]. Ashing temperatures up to 1400°C were possible using NaOH [57] or triethyl phosphite [58]. Probe atomization eliminated the need for chemical modification and standard additions calibration (aqueous standards were satisfactory) [59,60]. A Ta foil platform in a graphite tube was used for the standardless determination of Cd by Z GF AAS in a variety of matrices using various matrix modifiers [41,42]. Other metal atomizers included tungsten coil [25,61], Pt tube [62], Mo tube [63,64] or Mo-coated platform [46].

Atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 1–2 ng ml⁻¹ at the most sensitive 214.438 and 228.8 nm lines. They both suffer from spectral overlaps from Fe and Pt, and from As and Co, respectively, so ICP AES is usually used after a separation step [7,12]. The high volatility of Cd makes it suitable for ETV MIP AES (ADL of 10 pg) [65] and FANES [66,67].

Atomic fluorescence spectrometry

Flame AFS offered a DL of 20 ng ml⁻¹ [68]. It can be decreased to 0.2 ng ml⁻¹ [69] and 0.02 ng ml⁻¹ [30] by vapour phase introduction. Laser excited AFS is extremely sensitive (ADL 0.5 fg) for Cd [70–72].

Mass spectrometry

Cadmium has eight stable isotopes: ^{106}Cd (1.25%), ^{108}Cd (0.89%), ^{110}Cd (12.49%), ^{111}Cd (12.8%), ^{112}Cd (24.13%), ^{113}Cd (12.22%), ^{114}Cd

(28.73%) and ^{116}Cd (7.49%). Thermal ionization MS is based on the use of the ^{114}Cd for quantification and the ^{116}Cd as spike [24]. In ICP MS all major isotopes are overlapped by MoO ions [73,74] whereas $^{112}\text{Cd}^+$ and $^{111}\text{Cd}^+$ by ZrO ions [75]. Reduction of these interferences by cryogenic desolvation was proposed (DL 20 ng l^{-1} for ^{114}Cd) [74]. Electrothermal vaporization ICP MS has been reported for the measurement of Cd isotope ratios with a DL of 0.4 pg g^{-1} in biotissues [76].

Neutron activation analysis

This is based on the reaction: $^{114}\text{Cd}(n,\gamma)^{115}\text{Cd}$ and γ -counting of the ^{115}Cd ($t_{1/2} = 53\text{ h}$, $E_\gamma = 0.492, 0.528\text{ MeV}$) and offers a DL of *ca* 20 ng in the instrumental mode [77–79]. The DL can be improved by radiochemical separation [80]. *In vivo* NAA determination of Cd in soft tissues (liver and kidney) was reported [81].

20.3 ANALYSIS OF REAL SAMPLES

Analytical toxicology of Cd has been reviewed with particular attention given to environmental and biological samples [66,82–85]. The excellent overall performance of FAAS and its wide availability makes it the best suited technique for the analysis of geological materials and soils, usually after extraction into MIBK. In a variety of samples Cd is often determined in a multielement array as discussed in Part II. Contamination hazard is ubiquitous especially in the determination of Cd at the ng/ml or lower levels in clinical and environmental samples from pristine environments. Sources of contamination in terms of airborne particulates, sampling and storage equipment were discussed in detail with special attention to seawater [8] and clinical samples [86]. Common contamination sources are chemical modifiers [40]. A method for the removal of Cd contamination from a Pd–Mg matrix modifier by its pre-heating on the platform (to 1100°C) before the injection of the sample has been proposed [87].

Water

Direct GF AAS is readily feasible for waters with low salinity [88,89]. A comparison study showed that both off-wall atomization with an La matrix modifier and the STPF approach provided adequate accuracy [90]. Cadmium from fresh waters in conventionally preconcentrated by sorption [9,14,16,23,25,92]. In saline (e.g. seawater) samples, the salt matrix is volatilized at the same temperature as the metal which leads to a high background for which even the Zeeman correction is sometimes not

TABLE 20.1

Determination of trace cadmium in water samples

Water (amount)	Preconcentration/separation	Detection	DL (ng/l)	Ref.
Sea (0.35 l)	extraction with DDTc-APDC (Freon TF), back-extraction (HNO_3)	GF AAS	3.5	8
Sea (0.2–2 ml)	<i>on-line</i> sorption of the APDC complex on a C_{18} column	GF AAS	1.3	20
Sea	sorption on Chelex-100, pH 6.5, elution with 2 M HNO_3	GF AAS	n.g.	15
Sea (0.5 l)	coprecipitation of Cd-DBDTC complex with phenolphthalein	INAA	n.g.	77
Sea, river (0.2–0.5 l)	coprecipitation with PAN	GF AAS	1.5	18
River (0.1 l)	sorption by algal strain	GF AAS		23
River (0.05 l)	cathodic electrodeposition on a W wire	ETA AAS	10	25
River (0.1 l)	sorption on Pyrocatechol Violet or Xylenol Orange-loaded resin	FAAS	n.g.	16
Lake (2 l)	anion exchange as chloride complex, elution with 2M HNO_3	FAAS	5	21
Water (0.1 l)	coprecipitation with $\text{In}(\text{OH})_3$	GF AAS	2	91
Water (0.03 l)	cathodic electrodeposition	ID TIMS	1	24
Tapwater (1 l)	sorption on poly(dithiocarbamate) resin, elution with HNO_3	FAAS	30	14
Wastewater	sorption on iminodiacetate resin, elution with 1M HCl	ICP AES	50	12

sufficient [39]. An STPF GF AAS procedure using the $(\text{NH}_4)_2\text{HPO}_4$ - HNO_3 has been developed with a claimed DL of 5 pg ml^{-1} [48]. Separation of Cd, usually by extraction [8], coprecipitation [77] or sorption [15,18, 20], is often considered necessary. Analytical combined procedures for the determination of Cd in water are summarized in Table 20.1.

Clinical samples

Serum was analyzed after 2.5-fold dilution by STPF GF AAS with a DL of 0.14 ng ml^{-1} [51]. Cadmium in blood is fixed to haemoglobin and

metallothioneins [92]. Blood is commonly analyzed after dilution [50, 51] and/or deproteinization [66,68,93] by GF AAS. A 10-fold dilution was reported not to require a chemical modifier and D_2 correction was sufficient [43]. Matrix modification can be avoided and D_2 correction is sufficient after digestion of blood, serum and blood coagulum with $HNO_3-H_2O_2$ (ADL 7 pg) [92]. Results of an interlaboratory comparison of the determination of Cd in blood have been presented [94,95]. Quality assurance programmes have been described, the samples stored at $-20^\circ C$ for 5–6 years lost 5–10% of Cd although no adsorption to the container walls was detected [96]. The need for a reference material with extremely low concentration of Cd has been emphasized [97]. Urine can be analyzed directly after a 2–5-fold dilution with HNO_3 [98,99] or, more often, with a $Pd(NO_3)_2-NH_4NO_3$ matrix modifier [50, 51], with a DL of 0.1 ng ml^{-1} . Urine analysis with the pre-heated GF was faster [100]. Calibration with a metal-spiked human urine pool has been reported [31]. Probe atomization with D_2 background correction was recommended for rapid determination of elevated concentrations (DL of 0.3 ng ml^{-1}) in urine relevant to industrial exposure [59,60]. Acidification and addition of bactericidal agents is not a prerequisite for up to 10 days storage of urine [86]. Seminal fluid can be analyzed directly with a DL of 0.05 ng ml^{-1} [101]. Procedures for the analysis of clinical materials are summarized in Table 20.2.

Plant and animal tissues

The ease of Cd atomization makes solid sampling particularly attractive. Solid sampling followed by atomization from a platform with Zeeman background correction is the most popular for rapid screening of Cd [9,63,104–106]. Slurry sampling, especially after partial digestion, offers a better precision [23,107,108]. Dry ashing of tissue samples in a muffle furnace using a temperature control programme and relatively low temperature (up to $450^\circ C$) prevented loss of Cd by volatilization [33]. Combustion in O_2 for the determination of Cd in marine tissues has been discussed [40]. Wet digestion is generally preferred to dry ashing [109].

Foodstuffs

Foodstuffs are preferably analyzed as slurries by GF AAS with platform atomization; detection limits below 1 ng g^{-1} can be obtained [49,110,111]. Oxygen infusion facilitates *in-situ* ashing and avoids the build-up of carbonaceous residue in the tube [112]. Wet digestion procedures were found to be superior to dry ashing. Four digestion procedures for the determination of Cd in food samples by GF AAS have been

TABLE 20.2

Determination of cadmium in clinical samples

Sample (amount)	Decomposition (pretreatment)	Separation/pre-concentration	Detection	DL ($\mu\text{g/l}$)	Ref.
Blood	deproteinization with CCl_3COOH	extrn. with DDTC (MIBK)	FAAS	0.6	6
Blood	deproteinization with HNO_3	none	FANES	0.2	66
Blood, serum, coagulum (1 g)	$\text{HNO}_3, \text{H}_2\text{O}_2$	none	GF AAS	0.007 ^a	92
Blood, plasma, urine		anion exchange	GF AAS	0.1	102
Urine (20 ml)	HNO_3 or HClO_4 – HNO_3	electrodeposition on a W wire	ETA AAS	0.01	25
Urine	acidification with HNO_3	sorption on alumina, elution with HNO_3	FAAS	0.4	38
Urine (25 ml)	acidification with CH_3COOH	extrn. as CdI_4^{2-} with tri- <i>n</i> -octylamine (<i>n</i> -butyl acetate)	FAAS	1	1
SRM urine (1 ml)	none	electrodeposition	ICP MS	0.5	28
Human liver (1 g)	HNO_3 (microwave assisted)	none	FAAS	0.1 ^b	103

^a Absolute detection limit, ng; ^b in the sample, $\mu\text{g/g}$.

discussed, i.e. (i) H_2SO_4 – HNO_3 in an open flask, (ii) HNO_3 under pressure, (iii) H_2SO_4 – HNO_3 with refluxing and (iv) HNO_3 – HCl – H_2O_2 with refluxing; procedure (iii) was the best [113]. Microwave-assisted digestion *on line* [103] or in disposable autosampler cups [44] was fast and contamination free. Results of an interlaboratory comparison of the determination of Cd in mollusc tissue [114] and in calcium supplements and other Ca-rich matrices [115] have been reported. Procedures for the determination of Cd in non-clinical biomaterials are summarized in Table 20.3.

TABLE 20.3

Determination of Cd in biological samples

Sample (amount)	Decomposition	Separation/pre-concentration	Detection	DL (ng/g)	Ref.
BioCRMs	HNO ₃ (bomb)	sorption on 8-quinolinol loaded active carbon, elution with HCl	ICP AES	0.25 ^a	116
BioCRMs (0.1g)	HNO ₃ -HCl	ion exchange	RNAA	10	80
BioCRMs (0.3 g)	HNO ₃ (bomb)	<i>on-line</i> extrn. with DDTC (CCl ₄)	ICP AES	0.4 ^a	7
BioCRMs (1 g)	HNO ₃ (micro-wave assisted)	none	FAAS	100	103
BioCRMs (0.1 g)	HNO ₃ -H ₂ O ₂	none	GF AAS		63
BioCRMs (0.3 g)	HNO ₃ (bomb)	sorption on iminodiacetate resin, elution with 1 M HCl	ICP AES	0.05 ^a	12
BioCRMs	HNO ₃ -H ₂ SO ₄	sorption on dithizone-loaded charcoal, elution with MIBK	FAAS	0.3-1.3 ^a	17
Animal tissue (0.01-0.03 g)	HNO ₃ (bomb)		GF AAS	5	109
Animal tissue	HNO ₃	extrn. with dithizone (CCl ₄)	GF AAS		9
Tea infusions		volatn. as CdH ₂	ICP AES	1 ^a	32
Vegetables (40 g)	HNO ₃	extrn. with APDC (MIBK)	FAAS		5
Food, SRMs (1-3 g)	HNO ₃ -H ₂ SO ₄ -HClO ₄	extrn. as CdI ₄ ²⁻ (MIBK)	FAAS	10	1

^a In the solution fed, ng/ml.

TABLE 20.4

Selected methods for trace cadmium determination in industrial materials

Sample (amount)	Dissolution	Separation/pre-concentration	Detection	DL (ng/g)	Ref.
Silver	anodic	removal of the matrix by electrolysis	GF AAS	20	117
Indium (5–10 mg)	HNO ₃	extrn. of the matrix as InBr ₄ ⁻ (DIPE)	GF AAS	n.g.	3
Nickel (1–5 mg)	H ₂ SO ₄ –HNO ₃	extrn. of CdI ₄ ²⁻ with TOA (MIBK)	GF AAS	n.g.	3
Titanium oxide (0.5 g)	HF (bomb)	cation exchange	GF AAS	n.g.	118
High-purity reagents		<i>on-line</i> sorption of DDTC complex, elution with MeOH	GF AAS	70 ^b	19
Potassium chloride		electrodeposition on mercury	GF AAS	0.01 ^a	26
PVC (0.05–0.1 g)	H ₂ SO ₄ –H ₂ O ₂ , HNO ₃	none	FAAS	n.g.	119
PVC (4 g), organic salts (0.4 g)	DMF	complexation with calcein	FLU	1 ^a	120
Zinc (0.2–2 g)	HNO ₃	extrn. with dithizone (CCl ₄), DDTC (CCl ₄) or APDC (MIBK)	GF AAS	2000	121
Paper	HNO ₃ (bomb or wave assisted)	none	GF AAS	n.g.	122

^a In the solution fed, ng/ml; ^b in the sample solution, pg/l.*Industrial samples*

Analytical procedures developed solely for Cd are summarized in Table 20.4. Interlaboratory comparisons on the determination of Cd in wrapping paper samples [122] and in polyethylene [123] have been discussed. Cadmium was accurately determined in CRM polyethylene (in the range 40–400 mg kg⁻¹) by ID TIMS [124].

20.4 SPECIATION

Differentiation between Cd^{2+} , Cd chlorocomplexes, protein-bound cadmium and cadmium associated with colloids must be assured. Chemical separation methods for partitioning of Cd in sediments [125] and plant foodstuffs [126] have been described. Several operational methods for available Cd from soils based on leaching with different agents (CaCl_2 , DTPA- CaCl_2 -triethanolamine, ammonium acetate, *aqua regia*) usually followed FAAS or ICP AES determination have been developed [35,127-129]. Amberlite XAD-2 with In-saturated cation-exchange sites [130] and weak-base anion exchanger (diethylaminoethyl-Sephadex) [131] were capable of quantitative and fairly selective sorption of humic and fulvic complexes of Cd from fresh waters.

Considerable attention is attracted by the speciation of Cd metallothioneines (*cf.* Section 10.5) in animal tissues. Samples are homogenized with Tris-HCl, leupeptin and phenylmethylsulfonyl fluoride [132-134] or decomposed by enzymolysis [135,136]. Metallothioneins are thermally stable and the treatment at elevated temperature (70°C) in the presence of reducing agents (e.g. dithiothreitol) allows their full recovery [134]. Size exclusion chromatography is the most widely used separation technique whereas ICP MS the most popular determination technique. Analytical methods for speciation of Cd proteins are summarized in Table 20.5.

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TABLE 20.5

Speciation of Cd-thioneins

Sample	Decomposition	Chromatographic technique (eluent)	Detection	Ref.
Crab meat	enzymolysis with pepsin, pancreatin, amylase	reversed-phase (0.05% H_3PO_4)	UV	135
Animal liver, kidney		anion exchange (Tris-HCl buffer 0.01–0.25 M, pH 8.6)	GF AAS	137, 138
Pig kidney	enzymolysis with pepsin, pancreatin, amylase	size-exclusion (0.12 M Tris-HCl buffer, pH 7.5)	ICP MS	136, 139
Mussels	homogenization with Tris-HCl, leupeptin, phenyl-methylsulfonyl fluoride	size-exclusion (phosphate buffer, pH 7.5)	ICP AES	133, 134
Polychaete worm, proteins		size-exclusion (I: 0.06 M Tris-HCl buffer, pH 7.5, 0.05% NaN_3 ; II: 0.25 M NaCl, 0.06 M Tris-HCl buffer, pH 7.5, 0.05% NaN_3)	ICP MS	140
Rat and fetal bovine liver	homogenization with Tris-HCl, saccharose, 2-mercaptoethanol (pH 7.4)	reverse-phase (50 mM Tris-HCl buffer (pH 7.0) in MeOH)	AAS	141
Bean seeds, fruit	homogenization with water	ultrafiltration	GF AAS	54, 142
Mussels	homogenization with Tris-HCl buffer, NaN_3 , phenylmethane sulfonyl	anion exchange (0.1 M Tris-HCl buffer, pH 7.2)	FAAS	132
Mussels	homogenization with Tris-HCl buffer	size-exclusion (0.03% NaN_3 , 0.01 M Tris-HCl buffer, 0.1 M NaCl, pH 7.0)	UV	143
Rabbit liver		capillary zone electrophoresis (Tris-HCl buffer, pH 9.1)	UV	145
Cyano-bacterium	homogenization with Tris-HCl buffer, dithiothreitol, pptn. with $(\text{NH}_4)_2\text{SO}_4$, dissoln. in Tris-HCl buffer	size-exclusion (0.2 M $(\text{NH}_4)_2\text{SO}_4$, 0.05M Tris, 1 mM EDTA buffer, pH 7.5)	ICP MS	144

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Caesium

Caesium (atomic weight 132.91, melting point 28.5°C , $d = 1.87 \text{ g cm}^{-3}$) is a soft, highly reactive metal. It is moderately abundant in the earth's crust and occurs primarily in pollucite and rhodizite. Caesium is readily oxidized by air to form the hydroxide and carbonate, and reacts vigorously with H_2O and ethanol with evolution of H_2 . Most of the Cs salts are soluble in water. Caesium occurs in aqueous solutions as a monovalent cation, with no redox properties and only a weak tendency to form complexes with a restricted number of ligands, e.g. crown ethers. Determination of Cs is particularly demanded to evaluate environmental contamination by radioactive Cs isotopes resulted from nuclear weapon testing and nuclear power plants accidents.

21.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of Cs complexes with crown ethers containing more than 18 carbon atoms in the ring is the most popular. Lipophilic crown ether carboxylic acids with 21-crown-7 rings were found to exhibit good selectivity for Cs [1]. Dibenzo-24-crown-8 was used for separation of Cs from alkali, alkaline earth and many other metals [2]. High separation factors for Cs over Na were observed for extraction with dibenzo-18-crown-6 from trichloroacetate medium into 1,2-dichloroethane [3]. Extraction of Cs from alkaline solution with tetraphenylborate into di-iso-butyl ketone proved to be reliable whereas in acidic media polyvalent cations might affect the yield [4].

Sorption

Caesium can be separated from alkali and alkaline earth metals by extraction–chromatography on inert supports modified with crown ethers [5,6]. Sorption on freshly prepared Cu(II) hexacyanoferrate has been proposed for retention of ^{134}Cs and ^{137}Cs [7,8]. Sorption of ^{137}Cs on inorganic ion-exchangers based on Ti and Zr hydroxophosphates [9] or stannic silicomolybdate [10] is an alternative.

Precipitation

Caesium can be coprecipitated with KBPh_4 in an organic phase and stripped with acid [4]. Precipitation of Cs as molybdophosphate has been reported [11].

21.2 DETERMINATION TECHNIQUES

Atomic emission spectrometry

Flame AES offers a DL of 8 ng ml^{-1} in the recommended air– C_2H_2 flame at 852.1 nm [12]. Slurries can be nebulized [13]. Potassium interferes so its content must be closely matched in samples and standards or the method of standard additions has to be used for calibration [4]. The fuel-rich H_2 –air flame shows virtual freedom from inter-alkali interferences at the expense of poorer DL than in the air– C_2H_2 flame. Chloride interferes by promoting the formation of stable CsCl in the flame resulting in poor atomization efficiency [4]. The sensitivity of ICP AES is very poor.

Atomic absorption spectrometry

Vapour discharge or EDLs are used for Cs to offer DLs of $0.05\text{ }\mu\text{g ml}^{-1}$ and $0.01\text{ }\mu\text{g ml}^{-1}$, respectively, in an air– C_2H_2 oxidizing flame at the primary resonance line (852.1 nm) [12]. A red cut-off filter (below 650 nm) should be used. Potassium is used as an ionization buffer [14]. Graphite furnace AAS offers excellent detection limits (ca. 0.05 ng ml^{-1}) [12]. The sensitivity was reported to be improved by the addition of a large excess of KNO_3 but Zeeman background correction is required to compensate for the large non-specific background [15]. A detection limit of 2.3 ng ml^{-1} was reported with the use of a tungsten coil atomizer [16].

Nuclear methods

The Chernobyl accident triggered the need for contamination evaluation of fresh waters [7], foodstuffs [17], soil and grass [18]. The two

nuclides present ^{134}Cs and ^{137}Cs are determined by γ -counting. Preparation of calibration curve standards of ^{134}Cs and ^{137}Cs by serial dilution of a standard reference material has been proposed [19]. Irradiation of Cs yields short-lived $^{134\text{m}}\text{Cs}$ ($t_{1/2} = 3.2$ h, $E_{\gamma} = 0.128$ MeV) and long-lived ^{134}Cs ($t_{1/2} = 2.07$ y, $E_{\gamma} = 0.60$ and 0.79 MeV). Caesium can be determined after a certain decay time for decay of short lived nuclides. Sodium and potassium must be radiochemically removed if the short-lived $^{134\text{m}}\text{Cs}$ is used.

Other techniques

No reliable spectrophotometric methods for Cs determination have been reported in the literature. Laser-induced atomic ionization in flames offers an ADL of 2 fg [20,21]. Caesium has only one naturally occurring isotope ^{133}Cs . No interferences from polyatomic ions at this mass are expected in ICP MS [22,23].

21.3 ANALYSIS OF REAL SAMPLES

Environmental and geological materials

A significant number of studies evaluating the impact of the Chernobyl accident on the contamination of foodstuffs [17], soils [18], Alpine snow [24] and lake sediments [25] have been published. Caesium is often determined in a multielement array in fly ash by ICP AES [26,27] and INAA [26]. Caesium is the least concentrated of the alkali metals present in rocks. It is usually determined by FAAS [2], FAES [4,13] and GF AAS [14] directly after sample decomposition. Lithium hydroxide is a suitable flux for the basic and ultrabasic rocks [4] as the bulk of the rock matrix (except some Al and Cr) are left behind whereas Rb and other alkali metals pass into solution [4]. Adsorption of Cs on minerals has been reviewed [28].

Biological materials

Instrumental NAA has been used for the determination of Cs in clinical samples [29,30], plants [31] and foodstuffs [32] usually in a multielement array. There is very little risk of contaminating the serum sample with Cs, only careless separation of the serum from the packed cells or haemolysis may jeopardize the results [33]. Sampling techniques for radiocaesium in upland pasture and soil have been compared [34]. γ -Spectrometry is the most widely used technique for the determi-

nation of ^{137}Cs in mushrooms [36] and in milk powder [36]. Direct analysis of milk powder slurries has been reported [37].

Industrial materials

Flame AAS [38] and FAES are the most widely used techniques for the determination of Cs in high purity materials [13].

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Calcium and Magnesium

Calcium (Ca, atomic weight 40.01, melting point 845°C, $d = 1.55 \text{ g cm}^{-3}$) and magnesium (Mg, atomic weight 24.31, melting point 649°C, $d = 1.74 \text{ g cm}^{-3}$) are silvery-white lustrous alkaline earth metals. Both Ca and Mg are ubiquitous in the earth's crust with relative abundances of *ca* 4.7% and 2.8%, respectively. Both are biologically essential elements and are present at concentrations exceeding 0.01% up to subpercent levels in all kind of biological materials [1]. The need for the determination of low levels is restricted to some exocellular body fluids (<50 ppm) and materials where the metals had been artificially removed beforehand, e.g. high purity materials and water. Calcium and Mg are very similar in terms of analytical approach and will be discussed together. Both metals are chemically active and release readily H_2 from water and acids. Magnesium and calcium occur in aqueous solutions at the II oxidation state only, as the Ca^{2+} and Mg^{2+} ions. The hydroxides, $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, begin to precipitate at pH 9.6 and 12.7, respectively and show no amphoteric properties. The insoluble salts include fluoride, oxalate, carbonate and phosphate, those of Ca are less soluble. Magnesium and calcium form complexes with *O*-donor (tartrate, citrate, EDTA) ligands; those of Ca are more stable.

22.1 DETERMINATION

Separation and preconcentration

Magnesium and Ca (along with Sr and Ba) remain in solution while other elements are precipitated electrolytically or as hydroxides, sulphides, 8-hydroxyquinolinates or dithiocarbamates. Alternatively, Mg and Ca can be precipitated as hydroxides while amphoteric metals

remain in solution. Calcium may be precipitated as oxalate over a wide pH range (>3) [1]. There is no practical significance of extraction of the crown ether Ca complexes [2]. Sorption of Ca^{2+} on controlled pore glass-oxine has been discussed [3].

Atomic absorption spectrometry

Flame AAS offers very high sensitivity for both Mg (8 ng ml^{-1} at the 285.2 nm line) and Ca ($0.09 \text{ } \mu\text{g ml}^{-1}$ at the 422.7 nm line) in the recommended air- C_2H_2 , oxidizing (lean, blue) flame. The signal is suppressed by elements which give rise to stable oxysalts: Al, Be, Si, Ti, P, V and Zr. This effect can be reduced by the addition of 0.1–1% La or by use of the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame, recommended especially for samples rich in silica. Ionization should be controlled by adding an alkali metal salt, e.g. KCl. The phosphate and silicate interferences were also alleviated by the addition of $(\text{NH}_4)_2\text{MoO}_4$ or NH_4VO_3 [4] or of catechol or pyrogallol [5]. Graphite furnace AAS offers excellent detection characteristics (characteristic mass, DL) for Ca (0.8 pg, 0.05 ng ml^{-1}) and Mg (0.3 pg, 0.004 ng ml^{-1}). The practical use of this technique is restricted since background correction is cumbersome and contamination from the graphite furnace is significant, especially for Ca [6]. Further, Mg and Ca usually exist in the sample at levels amenable to FAAS.

Atomic emission spectrometry

Emission in the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame is sufficiently intensive to be applied analytically [7]. Inductively coupled plasma offers DLs of 0.1–0.5 ng ml^{-1} for Ca and Mg at the most sensitive 393.37 and 396.85 nm lines (Ca) [8–11] and 279.55, 280.27, 285.21 lines (Mg) [9–12] which show the virtual freedom from interferences at common levels in real samples. With a more sophisticated sample introduction system ADLs down to the 10 fg level have been reported [13]. A two-step excitation scheme for LEI was reported to give a DL of 0.02 ng ml^{-1} (with air- C_2H_2 flame) [14].

Mass spectrometry

Both Mg [^{24}Mg (78.99%), ^{25}Mg (10.00%) and ^{26}Mg (11.01%)] and calcium [^{40}Ca (96.94%), ^{42}Ca 0.65%, ^{43}Ca (0.136%), ^{44}Ca (2.09%) ^{46}Ca (0.004%) and ^{48}Ca (0.189%)] are multiisotopic and are amenable to TI MS. The $^{46}\text{Ca}:$ ^{48}Ca ratios have been measured and corrected for fractionation by iterative normalization (using the $^{44}\text{Ca}:$ ^{48}Ca ratio) [1]. In ICP MS the principal mass peak of ^{40}Ca is interfered with by $^{40}\text{Ar}^+$. A

less abundant peak ^{44}Ca (2.1% natural abundance) must be used instead. Magnesium isotopic ratios have been determined by ICP MS [15].

Other determination techniques

Magnesium cannot be readily determined by NAA because of the absence of a suitable nuclide. The determination of Ca is based either on the β -counting of the ^{45}Ca ($t_{1/2} = 164$ d, $E_{\beta} = 0.25$ MeV) formed in the reaction $^{44}\text{Ca}(n,\gamma)^{45}\text{Ca}$ or on the counting of ^{49}Sc ($t_{1/2} = 57$ min, $E_{\beta} = 2$ MeV) a decay product of the ^{49}Ca formed in the reaction $^{48}\text{Ca}(n,\gamma)^{49}\text{Ca}$. Since the abundances are small the sensitivity is not very high and the significance is restricted to the determination of Ca as part of a multi-element array. Spectrophotometric methods suffer from poor selectivity and require too much effort to be applied in trace analysis. Fluorescence of the calcein complexes of Ca and Mg at high pH in the FI mode has been proposed; 8-hydroxyquiniline was used to mask Mg and EGTA–Ca [16]. Energy dispersive XRF offers a DL of *ca* 70 ppm [17,18].

Analysis of real samples

Any preliminary procedural step should be avoided whenever possible because of the enormous contamination risk. Both Mg and Ca are usually determined in a multielement array primarily by FAAS or ICP AES which are precise and rapid. Examples of individual applications include the analysis of water [9], atmospheric deposits [10], brine [12], foetus bones [11], biological cells [13], gallium arsenide [19], REE oxides [16] and Al ceramics [20].

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Chromium

Chromium (Cr, atomic weight 51.996, melting point 1900°C , $d = 7.2 \text{ g cm}^{-3}$) is a silvery grey malleable metal. It is a relatively common element with an average concentration of 100 ppm in the earth's crust, occurring primarily in chromite (FeCr_2O_4) and krokoite (PbCrO_4). The metal is not attacked by HNO_3 because of passivation. It dissolves slowly in H_2SO_4 and more rapidly in HCl to form Cr(II) which is immediately oxidized to Cr(III) in the presence of oxygen. The oxidation states of practical importance are III and VI. Chromic hydroxide, Cr(OH)_3 which precipitates at $\text{pH} \sim 5$ is amphoteric. Chromium(III) forms inert complexes with oxalate, tartrate and EDTA. Strong oxidants, e.g. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (in the presence of Ag^+ as a catalyst) or KMnO_4 in acidic media, and peroxides and Na_2CO_3 on fusion or in alkaline media, oxidize Cr(III) to Cr(VI) . Chromium(VI) has oxidizing properties. The demand for trace analysis for Cr is particularly high in environmental and biological sciences; Cr(III) is an essential nutrient whereas Cr(VI) is toxic to plants, animals and man.

23.1 SEPARATION AND PRECONCENTRATION

Most chemical reactions of Cr are characteristic only of one of its oxidation states. Unless selective determination of Cr(III) or Cr(VI) is required (speciation), it is necessary to convert all the Cr to the reactive form, either by oxidation to Cr(VI) or by reduction to Cr(III) . Quantitative reactions may be, however, difficult at low levels and in complex matrices.

Coprecipitation

Traces of Cr(III) are precipitated as hydroxide in the presence of Fe(III) as a carrier [1–3] but Cr(VI) can partly adsorb onto the precipitate [4]. Chromium(VI) can be separated by coprecipitation with BaSO₄ or PbSO₄ [5] or with various dithiocarbamates [2,3,6]. Electrodeposition [7,8] and bioprecipitation of Cr (principally Cr(VI)) on algae [9] have been reported.

Extraction

Chromium(III) is only slowly extracted with acetylacetone, but much faster with its fluorinated derivatives, e.g. trifluoroacetylacetone, into non-polar solvents [10–12]. Anionic complexes of Cr(III) with SCN[−] or DCTA are readily extracted into CHCl₃ in the presence of an ion-pairing agent. Selective extraction of Cr(III) with 8-hydroxyquinoline (MIBK) has been reported [13]; the complex formation can be accelerated by microwave heating [14]. Chromium(VI) can be selectively extracted with MIBK from 1–3 M HCl (only In, Tl, Sb, Hg, W and Re interfere) [15,16]. Inert solvents (e.g. CHCl₃, C₆H₆, 1,2-dichloroethane) extract ion-associates of chromate with high molecular weight amines and tetraalkylammonium salts from acid media [7,17–19]. Chromium(VI) is also readily extracted from weakly acidic solutions with dithiocarbamates into various solvents [19–23].

Sorption

Chromium(III) is generally not retained on anion exchangers from 0.02–12 M HCl and thus it can be separated from many metals that form chloride complexes. Anionic forms of Cr(III) can be retained from less acidic media and eluted with strong acids [24]. Cation exchangers [25–27] and some chelating resins [28–30] retain Cr(III) but not Cr(VI). Conversely, Cr(VI) is selectively retained on strongly basic anion exchangers [24,26,31–36] and can be eluted with NH₃(aq) [24,31,32] or with hydroxylamine [33,37]. Chromium (VI) was selectively retained on C₁₈ disposable cartridges loaded with tributyltin [38]. Alumina was shown to have a strong preference for anionic forms of Cr from acid media [24,32,39]; Cr(III) either was not retained or could readily be eluted with HNO₃. Sorption of the Cr complexes with dithiocarbamates [40,41] or 8-hydroxyquinoline [14] has been reported. Simultaneous preconcentration of Cr(VI) and the Cr(III)–EDTA complex on anion-exchanger at pH 4–6 has been developed [42].

Volatilization

Chromium(VI) can be distilled as CrO_2Cl_2 from HClO_4 at 200°C . Volatilization of Cr- β -diketonate complexes (with acetylacetone or trifluoroacetylacetone) has been reported [43,44].

23.2 DETERMINATION

Spectrophotometry

Reaction of Cr(VI) with 1,5-diphenylcarbazide at pH 1 is the basis of a sensitive ($\epsilon = 4.3 \times 10^4$ at 545 nm) and fairly selective method. Sensitivity can be increased by solid phase spectrophotometry [45]. Large amounts of Fe(III) interfere and must be masked by EDTA or H_3PO_4 . The oxidation of Cr(III) to Cr(VI) is normally done in acid medium with Ce(IV), KMnO_4 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of Ag^+ [46–48]; the excess of the oxidant is decomposed by boiling with azide. Interferences from Cr(V) [49] and H_2O_2 [50] have been discussed. The method is commonly used for post-column detection of Cr(VI) in LC [31], and is applied in FI mode for total Cr [46] and for speciation Cr(VI) and total Cr [47,48]. Despite being continuously published, other methods have not matched the overall performance of the diphenylcarbazide method despite sometimes higher sensitivity, e.g. the determination of Cr(VI) with *o*-nitrofluorone and CTA ($\epsilon = 1.1 \times 10^5$ at 582 nm) [51].

Chemiluminescence

Chromium(III) catalyzes oxidation of luminol by H_2O_2 [27,52–54] or pyrogallol with periodate [55] which forms the basis of a sensitive (DL $\sim 1 \text{ pg ml}^{-1}$) method, adaptable to FIA [52]. EDTA is used as a masking agent, especially for Fe(III) [27,52].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.08 \text{ } \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 flame (reducing, rich, yellow) at the most sensitive 357.9 nm line. The common interferences include signal enhancement due to Al, Ca, Mg, signal suppression due to Fe and Ni and both effects due to the presence Mn, K, Na, Cu in proportions dependent on the Cr chemical form. The interferences can be almost completely eliminated in an $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame at the expense of sensitivity [15,56]. The latter can be increased in the presence of thiocyanate [57] or by extraction with MIBK [16]. Quartz furnace AAS determination of volatile chromium β -diketonate complex offered a 50-fold higher sensitivity than conventional FAAS [43].

Graphite furnace atomic absorption spectrometry

Uncoated, pyrolytic graphite coated and totally pyrolytic graphite atomizers were compared; the latter provided the best sensitivity (<1 pg) [58] which can be increased by pre-heating the tube [13,59]. Pyrolytically coated tubes are used to prevent the formation of carbides [60–62]; the quality of the coating is of paramount importance. Tantalum carbide coated [63] or W-impregnated tubes [64] were proposed to offer higher sensitivity and longer tube lifetime. Formation of stable carbides was alleviated by the use of HNO_3 , $\text{Mg}(\text{NO}_3)_2$ and Na_2WO_4 [13] and V(V) and V(V)–Mo(VI) [65] as matrix modifiers. The effect of alkali and alkaline earth metals on the atomization of Cr has been discussed [66]. Extraction was used to remove interferences due to high contents of Na, Ca, K and Mg [1,17,18]. Injection of chlorine was used to abolish carryover from chromium carbide [67]. Losses of Cr are common during ashing below 800 K in the presence of chloride owing to the formation of volatile CrCl_3 [68]. Mechanisms of vaporization of Cr using ETV have been studied [69]. Different atomization techniques (wall, platform and probe) have been compared; wall atomization and an Mg–Ca– NO_3 matrix modifier provided a DL of 0.05 ng ml^{-1} [60]. The ashing stage can be eliminated by the use of a short temperature programme [70,71]. The hot injection mode was reported to improve the sensitivity [72].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers DLs of $3\text{--}5 \text{ ng ml}^{-1}$ at the most sensitive 205.55, 206.15, 267.72 and 283.56 nm lines. Electrothermal vaporization ICP AES was found to be capable of determining Cr levels down to $0.5\text{--}1.5 \text{ ng ml}^{-1}$ [73,74]; PTFE-assisted vaporization has been reported [74]. The 283.56, 267.72, and 206.15 nm lines are interfered with by Fe, Mn, and Zn respectively. Separation of Cr from Ca and Mg is essential to avoid stray light and ion–electron recombination emission [75]. Use of DCP AES has been discussed [24,76].

Mass spectrometry

Chromium has four naturally occurring isotopes: ^{50}Cr (4.34%), ^{52}Cr (83.79%), ^{53}Cr (9.50%) and ^{54}Cr (2.36%). Thermal ionization MS, EI MS and ICP MS are all widely used. In TI MS the most abundant ^{52}Cr nuclide is measured whereas ^{53}Cr is added as the spike [7,8,35]. Separation of Cr from the matrix, e.g. by electrodeposition or anion exchange is necessary [7,8,35]. Volatile Cr chelates with TFA [11] or bis(trifluoroethyl)-DTC [23] can be determined by GC ID MS (^{50}Cr is added as

the spike) with an ADL of 0.03 ng. In ICP MS the ^{50}Cr and ^{54}Cr nuclides are overlapped by $^{35}\text{Ar}^{14}\text{N}^+$ and $^{38}\text{Ar}^{16}\text{O}^+$, respectively [31], and thus only the isotopes ^{52}Cr and ^{53}Cr are of analytical utility. The background at mass 52 ($^{36}\text{Ar}^{16}\text{O}^+$) is significantly higher than that at mass 53 ($^{36}\text{Ar}^{17}\text{O}^+$, $^{36}\text{Ar}^{16}\text{O}^{1}\text{H}^+$) which largely offsets the abundance advantage of the ^{52}Cr isotope. Additional interferences for ^{52}Cr can arise when samples contain high concentrations of carbon (overlap with $^{40}\text{Ar}^{12}\text{C}^+$) or sulphur ($^{36}\text{S}^{16}\text{O}^+$) [31,77]. When ICP MS is used as a detector in SFC the CO_2 mobile phase should thus be replaced by N_2O to avoid the spectral interference [77]. The ^{53}Cr can be overlapped by $^{37}\text{Cl}^{16}\text{O}^+$ when high concentrations of chlorine are present [31]. Anion exchange was proposed to remove spectral interferences due to sulphur and chlorine [78]. An ICP mass spectrometer is a useful detector for HPLC to offer a DL of 1–3 ng ml $^{-1}$ for ^{52}Cr and ^{53}Cr [31]. Isotope dilution RI MS has been discussed [79].

Neutron activation analysis

This is based on the reaction $^{50}\text{Cr}(\text{n},\gamma)^{51}\text{Cr}$ and counting the 320 keV γ -photopeak of ^{51}Cr ($t_{1/2} = 27.8$ min). Mercury ($E_\gamma = 0.320$ MeV) interferes and should be separated. Interference with ^{54}Fe was evaluated by monitoring the reaction $^{54}\text{Fe}(\text{n},\text{p})^{54}\text{Mn}$ [80]. Radiochemical NAA offers a DL of 5–10 pg Cr [6,28,81].

X-Ray fluorescence

The accurate measurement of the Cr $K\alpha$ photopeak is hampered by the large background continuum and the overlaps from the iron $K\alpha$ and Ti $K\beta$ photopeaks which elements are usually present in a few orders of magnitude excess to Cr. Counting times for ED XRF were optimized to prevent the iron overlap often at the expense of precision [82]. A Co anode X-ray tube was shown to overcome many of these problems; the fluorescence of iron K lines was selectively suppressed (DL 6 ppm) [82]. The changes in peak positions and profile in the X-ray emission lines of Cr in several oxidation states and ligand environment have been employed in the determination of the ratio of Cr(VI) to total Cr [83]. Prior to XRF Cr is usually separated from the matrix [2,3].

23.3 SPECIATION

Discrimination between Cr(VI) and Cr(III) is crucial in the analytical chemistry of Cr. The redox equilibrium between Cr(III) and Cr(VI) is sensitive to pH changes and to addition of oxidizing or reducing agents.

This vulnerability has restricted speciation studies to water samples where neither matrix destruction nor aggressive leaching is necessary. Speciation approaches are based either on selective determination of Cr(III) or Cr(VI) or on chromatographic separation of Cr(III) and Cr(VI). Both approaches can be realized *off line* or *on line*, often in FI mode. The more toxic Cr(VI) species was unstable and most of the Cr(III) is associated with macromolecular particles in wastewater samples [10]. Speciation schemes to distinguish between stable complexes, colloidal fraction, Cr bound to macromolecular fraction and Cr(III) and Cr(VI) for wastewater samples have been discussed, but the methods used (extraction, ultrafiltration, ion exchange) shifted the equilibrium state so the initial concentrations in the samples could not be determined [10].

Storage

Storage problems include reduction of Cr(VI) under acid conditions [5,49,50]. No losses of the total dissolved Cr by precipitation or adsorption on the container walls were observed for water samples stored at natural pH in polyethylene bottles for 14 days [5]. It was found that the $\text{HCO}_3^-/\text{CO}_2$ buffer keeps Cr(III) stable for 160 days at 5°C and Cr(VI) for at least 120 days [7]. Avoiding loss of CO_2 is essential for the stability of Cr(III); storage under a CO_2 blanket has been recommended [7].

Differential methods

Single-species-selective methods include spectrophotometry [45] [usually for Cr(VI)] or chemiluminescence [52] [for Cr(III)], selective volatilization GF AAS [64] and XRF [83]. An optimization of the separation conditions enables each of the species to be determined [2,3,6,21]; selective separation techniques were discussed in Section 23.1. The different behaviour of Cr(III) and Cr(VI) on ion exchangers is the most common method for their separation in speciation studies [24,25,27,32,33,37,53,76]. It is more common to determine either Cr(III) or Cr(VI) whereupon the concentration of the other species is calculated as the difference from the total Cr [14,22,39,47,48]. Several methods based on splitted-stream FI systems (*cf.* Chapter 7.7), in which Cr(VI) and total Cr upon oxidation to Cr(VI) are determined, have been developed [40].

Chromatographic methods

In the simplest approach both species are retained, e.g. on activated alumina and subsequently selectively eluted with 0.02 M HNO_3 for Cr(III) and 1 M NH_3aq for Cr(VI) [24]. Complexes of Cr(III) and Cr(VI)

with APDC have been separated by reversed-phase chromatography [84]. Anion exchange can be used for differentiation of Cr(VI) and Cr(III) associated with negatively charged colloids [33]. Otherwise conversion of Cr(III) to an anion, e.g. by complexation with SCN^- , $\text{Cr}(\text{SCN})_4^-$, pyridine dicarboxylic acid $\text{Cr}(\text{PDCA})_2^-$ or EDTA, is required. In ion interaction chromatography ion pairs formed by Cr(III) [converted into the acetate complex to avoid precipitation] with $(\text{Bu}_4\text{N})_3\text{PO}_4$ and Cr(VI) (present as CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$) with TBA are separated [85–87]. Chromatographic methods, especially SFC, are the only methods for speciation of organochromium (β -ketonate Cr(III) compounds). Chromatographic methods for speciation of Cr are summarized in Table 23.1.

23.4 ANALYSIS OF REAL SAMPLES

Chromium contents in ores well exceed the 100 ppm level; the concentrations in rocks are usually determined in a multielement array (*cf.* Chapter 9). Chromium is determined in a variety of alloys but seldom at trace levels. The largest interest is in the determination of Cr in environmental waters and biological, especially clinical, materials. Biological and environmental aspects of Cr have extensively been discussed [91–93].

Water

The Cr content in surface waters is typically between 0.3 and $6\ \mu\text{g l}^{-1}$. Total chromium is usually determined directly with GF AAS (DL ca. $0.1\ \mu\text{g l}^{-1}$) [65,94]. Magnesium nitrate and Na_2WO_4 have been recommended as matrix modifiers for salt-rich and salt-poor matrices, respectively [94]. Selective reaction of Cr(VI) with diphenylcarbazide is widely used for spectrophotometric analysis of waste waters or for solid phase spectrophotometry of fresh waters [45]. The Cr species most frequently found in river and lake water as CrO_4^{2-} , cationic hydroxocomplexes, such as $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_2^{2+}$, and organically bound or colloiddally sorbed Cr(III) [33,37]. In seawater Cr(VI) should dominate but a small fraction of kinetically inert Cr(III) is present as well. The conditions necessary for simultaneous determination of Cr(III) and Cr(VI) are critical because Cr(VI) is vulnerable to reduction in acidic solution [53,87] whereas Cr(III) is easily hydrolyzed above pH 3 [53]. An operational procedure to distinguish between Cr(VI), free Cr(III), complexed Cr(III) and particulate Cr in fresh waters based on coprecipitation with lead

TABLE 23.1

Chromatographic methods for speciation of chromium

Species	Sample	Separation technique	Detection technique	DL (µg/l)	Ref.
Cr(III), Cr(VI)	galvanic waste waters	RPC of APDC complexes in ethyl acetate extract	UV	~2	84
Cr(III), Cr(VI)	drinking, waste water	IIC of ion pairs with $\text{CH}_3\text{COONBu}_4$ in acetate medium	FAAS	0.03–0.5	85
Cr species	liver tissue, plasma	SEC or cation exchange chromatography	UV	n.g.	88
Cr species	liver tissue, plasma	anion exchange chromatography	UV	n.g.	34
Cr(III), Cr(VI)	spiked pond water	IIC of ion pairs with $(\text{Bu}_4\text{N})\text{PO}_4$ in acetate medium	FAAS	0.04–0.08	87
Cr(III), Cr(VI)	standards	IC	CL	0.05–0.1	53
Cr(VI)	drinking, groundwater, wastewater	sorption of Cr(VI) on anion exchanger	VIS	n.g.	36
Cr(VI)	soil extracts	IIC of ion pairs with $(\text{Bu}_4\text{N})\text{PO}_4$ in acetate medium	GF AAS	0.3	86
Cr(VI)	spiked pond water	IIC of ion pairs with $(\text{Bu}_4\text{N})\text{PO}_4$ in acetate medium	FAAS	0.8	89
β -Ketonate Cr(III) complexes	standards	SFC with N_2O mobile phase	FID; ICP MS	10–250 ^b ; 1–3 ^b	77
-Ketonate Cr(III) complexes	standards	SFC with 20% MeOH in CO_2 mobile phase	UV	n.g.	90

^a Anion exchanger with small proportion of cation exchange groups.^b Absolute detection limit, pg.

RPC = reversed-phase chromatography; IC = ion-chromatography; IIC = ion interaction chromatography; SFC = supercritical fluid chromatography.

salts followed by GF AAS has been developed (DL 0.03–0.15 ng ml⁻¹ [4]). It is not possible to equate anion-exchangeable Cr with Cr(VI) since the Cr(OH)₄⁻ anion is the predominant anion, e.g. in seawater and Cr(III) is sorbed by negatively charged colloids in river waters. Methods for the determination of Cr in waters involving a preconcentration step are summarized in Table 23.2. Speciation chromatographic methods can be found in Table 23.1.

TABLE 23.2

Determination of chromium in water

Species	Water (amount)	Separation and/or preconcentration	Detection technique	DL (µg/l)	Ref.
Cr(III)	sea	sorpn. on poly(hydroxamic acid) resin; eln. with 1 M HCl	FI FAAS		29
Cr(III); Cr(VI)	CRM	sorpn. of Cr(III) on alumina (pH 7), eln. with 1 M HNO ₃ ; sorpn. of Cr(VI) at pH 2, eln. with 0.5 M NH ₃ (aq)	FI FAAS	1	39
Cr(III); Cr(VI)	CRM	sorpn. of Cr(III) by cation exchange; eln. with 0.1 M K ₂ SO ₄ (pH 3); Cr(VI) not retained	CL	0.5	27
Cr(VI); Cr(total)	natural	sorpn. of Cr(VI)–DDTC complex on C ₁₈ ; total Cr detn. after oxidation of Cr(III) with K ₂ S ₂ O ₈ , eln. with EtOH	FI GF AAS	~0.02	40
Cr(III); Cr(VI)	CRM	sorpn. of Cr(VI) by anion exchange; eln. with 1 M NH ₃ (aq); Cr(III) not retained	ICP AES	0.2–1.4	32
Cr(III); Cr(VI)	lake (0.2 l)	sorpn. of Cr(III) on CE, elution with 1 M NH ₄ NO ₃ – 0.1 M HNO ₃ ; sorption of Cr(VI) by anion exchange; eln. with 5 M HNO ₃	GF AAS	0.02	26
Cr(III); Cr(VI)	fresh	extrn. of Cr(VI) with Amberlite LA-2 (MIBK), back-extrn. (NH ₃ (aq)), electrodeposition	ID TMS	1–2	7
Cr(VI)	river	selective volatn. of Cr(III)–TFA complex from the graphite furnace prior to the detn. of Cr(VI)	GF AAS		44

continued

TABLE 23.2 *continuation*

Species	Water (amount)	Separation and/or preconcentration	Detection technique	DL ($\mu\text{g/l}$)	Ref.
Cr(III); Cr(VI)	CRM fresh	sorpn. of Cr(III) on CE; sorpn. of Cr(VI) on AE; reductive eln. with K_2SO_3	CL	0.1– 0.3	54
Cr(VI); Cr (total)	sea (0.2 l)	extrn. of Cr(VI) with DDTC (CHCl_3) at pH 4.0, back-extrn. [Hg(II)]; detn. of total Cr after oxidn. with KMnO_4	GF AAS		22
Cr(total); Cr(VI)	tap, well, river	sequential extrn. with APDC (MIBK)	GF AAS	0.3 ^a	21
Cr(III); Cr(VI); Cr (total)	sea, well, tap	copptn. of Cr(VI) with $\text{Pb}(\text{APDC})_2$ at pH 4.0; copptn. of Cr(III) with $\text{Pb}(\text{APDC})_2$ at pH 9.0; total Cr after reduction with NaHSO_3	NAA	0.03	6
Cr(III); Cr (total)	sea	sorpn. of Cr(III)-8-hydroxyquino- line complex; total Cr after reduction with NH_2OH	GF AAS	0.001– 0.002	14
Cr(tot)	CRM sea (5 ml)	sorpn. of the CMDTC complex; elution with $\text{NH}_3(\text{aq})$	ICP MS	0.04	41
Cr(VI)	fresh	matrix removal by cation exchange; sorption of the Cr(VI)– diphenylcarbazide complex	FI-SP VIS	0.5 ^a	45
Cr(VI)	river, sea, waste	copptn. with PbSO_4 at pH 3.5	GF AAS	0.3	5
Cr(III); Cr(total)	sea	copptn. of Cr(III) with $\text{Ga}(\text{OH})_3$; Cr(total) after redn. with NH_2OH	GF AAS	0.02	114
Cr(III); Cr(VI)	sea (2×0.1 l)	copptn. of Cr(VI) with Co–PDTC at pH 4.0; copptn. of Cr(III) with $\text{Fe}(\text{OH})_3$ at pH 8.5	XRF	0.13	3
Cr(VI); Cr(III)	river (0.2 l)	sorption by anion exchange; eln. of Cr(VI) with 5% $\text{NH}_2\text{OH} \cdot \text{HCl}$; eln. of Cr(III) with 4 M HNO_3	GF AAS	0.01	37
Cr(III); Cr(VI); Cr(col)*	lake (0.5 l)	sorpn. by anion exchange; I: 5% NH_2OH ; II: 4 M HNO_3	GF AAS	0.004– 0.02	35

^a Absolute detection limit, ng. * Associated with colloids.

Geological samples

Chromium present in refractory chromite is not released by hot concentrated HNO_3 so an HF-HClO_4 attack, hot H_3PO_4 leaching or alkali fusion is required [56]. Three analytical techniques have been compared for the determination of Cr(VI) in soil extracts; ion-interaction HPLC GF AAS was found to be the most suitable (DL 0.3 ng ml^{-1}) [86]. Anion-exchange ICP MS (DL 1 ng ml^{-1}) is a more expensive alternative [31]. Spectrophotometry with 1,5-diphenylcarbazide was not applicable to the analysis of most extracts owing to its high DL (30 ng ml^{-1}) and the possibility of the instantaneous reduction of Cr(VI) under the acidic conditions employed [86]. Light scattering on colloidal particles can produce severe positive systematic errors in the spectrophotometric determination of Cr(VI) in soils containing a large clay fraction [86]. The separation of Cr(VI) on a Chelex-100 column was inclined to give higher results as inert and moderately labile Cr(III) complexes partially passed the resin together with Cr(VI) [86]. Soil extracts (extraction with EDTA) required the destruction of Cr-EDTA before the oxidation-extraction procedure [15].

Clinical samples

Determination of Cr in clinical samples has been reviewed [95]. Serum [28,58,67,96–98] and cerebrospinal fluid [99] are generally analyzed after 1+1 dilution with Triton X-100 (sometimes with HNO_3 [72,99], $\text{Mg}(\text{NO}_3)_2$ [96] or Mg-Ca-NO_3 [60], V(V)–Mo(VI) [65]) as matrix modifiers with a DL of $0.1\text{--}0.2 \text{ ng ml}^{-1}$. A larger (2–5-fold) dilution is required for the whole blood [100–102]. Oxygen was added to support ashing of erythrocytes in the graphite furnace [103]. Calibration is done with matrix matched standards [101]. Enzymatic pretreatment with bacterial protease was proposed to liberate protein-bound Cr in serum and plasma [96]. The normal urine concentration is ca. $1 \mu\text{g l}^{-1}$ which is ten-fold higher than the normal blood level [70]. Urine is usually analyzed with no dilution with a DL of $0.05\text{--}0.2 \text{ ng ml}^{-1}$ [28,60,100,101] but 1+1 dilution with a mixture of dilute HNO_3 and Triton X-100 is safer in terms of accuracy at the expense of sensitivity [70,97,104,105]. The background is usually within the range suitable for D_2 -correction [70, 99] but Zeeman correction is often used [28,70,96,100, 104]. Careful optimization of the program is necessary to alleviate the effect the potassium interference occurring at three different Cr wavelengths: 357.9, 359.4 and 425.5 nm [106]. Calibration is done with matrix-matched standards [101] or Cr-spiked human urine pool [100]. Gas

chromatography ID MS has been used for the accurate determination of Cr in urine [11,23]. Normal values for Cr in human pulmonary tissue have been discussed [107].

Plant and animal tissues

Food [108], plant [71] or animal tissue [109] digests have been analyzed by AAS directly or upon dilution with D_2 background correction. Substantial losses of Cr due to the adsorption of silica were observed during plant digestion by HNO_3-HClO_4 , dry ashing followed by removal of silica (with HF) gave accurate results [15]. Removal of silica from plant samples digests was found necessary [1]. Bioavailable chromium was extracted from foodstuffs with ethanol [108]. Direct determination of Cr in the milk powder using Triton-100 or $Mg(NO_3)_2$ was reported to give a DL of 5 ng g^{-1} [110]. Combined analytical procedures for the determination of Cr in biological tissues are summarized in Table 23.3.

Accuracy considerations

Contamination is a real hazard in the analysis of natural waters and clinical materials. Class 100 environment and class 1000 portable field clean benches for initial sample handling are essential [37,101]. Care to avoid contamination during sample collection and storage has been advocated; glass containers and coagulants were found to contribute to the blank and plastic storage containers were preferred [58]. Stainless steel equipment must be avoided; Cu-Be alloyed knives were proposed to collect the samples [106]. Interlaboratory exercises on the determination of Cr in timber treated with preservative [111], plant tissues [1] and biological materials [112] have been summarized; possible sources of error were discussed. Development and interlaboratory testing of aqueous and lyophilized reference materials for Cr speciation are in progress [112]. The results of a collaborative study on an ion-chromatographic method for dissolved Cr(VI) in drinking water and groundwater and industrial wastewater effluents have been presented [36].

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TABLE 23.3

Determination of chromium in biological materials using combined procedures

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection technique	DL (ng/ml)	Ref.
Urine (1 ml)	HNO ₃ , H ₂ O ₂	extrn. with bis(tri-fluoroethyl)-DTC (CH ₂ Cl ₂); GC	ID MS		23
Urine (3 ml)	HNO ₃ , H ₂ O ₂	extrn. with TFA (hexane); GC	ID MS	0.03 ^a	11
Urine CRM	none	sorption of Cr(III) on alumina; eln. with 2 M HNO ₃	FI ICP AES	0.05	75
Urine CRM	none	sorption of the bis(carboxymethyl)-DTC complex on inert support	ICP MS	0.04	41
Urine (10 ml)	HNO ₃ -H ₂ SO ₄	extrn. with N-235 (benzene)	GF AAS	0.01	17
Urine (0.5 ml), serum (0.5 ml)	HNO ₃ (microwave assisted)	sorption on Cellex-P after reduction with ascorbic acid	RNAA	0.03	28
Foodstuffs (5-10 g)	HNO ₃	oxidn. with KMnO ₄ , extrn. of Cr ₂ O ₇ ²⁻ (MIBK)	FAAS	3.8	16
BioCRMs (0.2 g)	HNO ₃ -HClO ₄	extrn. of Cr(VI) with TBA (CHCl ₃); back-extrn. (NaOH soln.); anion exchange of Cr(VI)	RNAA	few ^a	81
Plants	HNO ₃ -HClO ₄ -H ₂ SO ₄	reduction with Na ₂ SO ₃ , copptn. with Fe(OH) ₃ , extrn. of FeCl ₄ ²⁻ (MIBK), evaporation of SiF ₄ with HF	GF AAS	n.g.	1
Plant CRMs (2-5 g)	dry ashing with H ₂ SO ₄ , evapn. with HF	oxidation with (NH ₄) ₂ S ₂ O ₈ , extrn. into MIBK	FAAS	n.g.	15
Plant CRMs (0.5-1 g)	HF-HNO ₃	anion exchange separation after oxidation	ID TIMS	0.5	35

^a Absolute detection limit, ng.

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Cobalt

Cobalt (Co, atomic weight 58.93, melting point 1493°C, $d = 8.9 \text{ g cm}^{-3}$) is a hard lustrous ferromagnetic metal. It occurs in the earth's crust with an average abundance of 18 ppm, primarily as smaltite (CoAs_{2-3}), cobaltine (CoAsS) and linneite (Co_3S_4) in sulphidic Cu ores and pyrites. The metal dissolves slowly in dilute mineral acids but rapidly in concentrated HNO_3 . In aqueous solutions Co exists mainly in the II oxidation state as the pink Co^{2+} ion but in some complexes Co(II) is readily oxidizable to Co(III). The hydroxide, $\text{Co}(\text{OH})_2$, which precipitates at pH ~ 7.5 is insoluble in excess NaOH but dissolves in $\text{NH}_3(\text{aq})$. Cobalt forms stable ammine, cyanide, tartrate, citrate and EDTA complexes. Cobalt is an important component of steels and ferromagnetic alloys. Biologically Co is an essential element being a component of vitamin B_{12} . Cobalt belongs to the group of occupational carcinogens. The nuclides ^{60}Co , ^{58}Co and ^{57}Co are products of nuclear weapon testing and are environmental contaminants.

24.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of Co with 2-nitroso-1-naphthol at pH 4.5 into inert solvents (CHCl_3 , heptan-2-one, xylene) is popular because of its selectivity [1–3]. Alternatively, Co can be extracted with APDC into MIBK [4–6] at pH 4–4.5 after removal of Fe (e.g. by extraction with cupferron at pH 1.3) [4,6]. A large enrichment factor (>500) was reported with a liquid surfactant membrane [7].

Precipitation

Precipitation of traces of Co as Co(OH)_2 with La, Al or Fe(III) as collectors is well established. Chelating agents, e.g. 8-hydroxyquinoline (with Mg as carrier) [8] and 1-nitroso-2-naphthol [9] (in *on-line* mode) have also been proposed. Coprecipitation of Ni and Fe can be prevented by adding citrate [9]. Ion and precipitate flotation of Co(II) in the presence of cationic and anionic surfactants has been reported [10].

Sorption

Sorption of Co on chelating resins, e.g. Chelex-100 [11] or resins functionalized with nitroso-R salt [12] or 8-hydroxyquinoline [13] is widely practised. Alternatively, reagent (nitroso-R salt [14,15], TOPO [16]) loaded resins can be used or Co can be retained as the complex with nitroso-R-salt [17] or various dithiocarbamates on inert supports [18,19]. Anion exchange from concentrated HCl [20] and thiocyanate media [21] has been reported. Sorption preconcentration is conveniently applied in FI mode [14,15,19].

Volatilization

Trifluoroacetone was found to be the most suitable from different β -ketones and dithiocarbamates evaluated for the volatilization of Co from aqueous media [22].

24.2 DETERMINATION TECHNIQUES

Spectrophotometry

1-Nitroso-2-naphthol ($\epsilon = 2.9 \times 10^4$ at 415 nm) and its isomer 2-nitroso-1-naphthol ($\epsilon = 3.7 \times 10^4$ at 365 nm) react with Co(II) in a similar, highly selective manner to form chelates soluble in non-polar solvents (usually CHCl_3). The reaction is fairly slow and takes 30 min to complete. The Co complex is stable and does not decompose while other metals, e.g. Ni, Cu, Fe and Cr are stripped from the organic phase with 2 M HCl. Larger amounts of Fe(III) are either masked with fluoride or pre-extracted. The disulphonic derivative of 1-nitroso-2-naphthol (nitroso-R salt) forms with Co a water-soluble colour complex ($\epsilon = 3.5 \times 10^4$ at 415 nm). A chemiluminescent method based on the catalytic effect of Co on the oxidation of gallic acid in an alkaline H_2O_2 medium was proposed; pre-separation of Co was required [13].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of 0.1 mg l^{-1} at the most sensitive 240.7 and 242.5 nm lines in the recommended air-C₂H₂ flame (oxidizing, lean, blue). Excess of some metals depresses the Co signal so matrix matching of standards is important. Flame AAS is often preceded by a separation-preconcentration step [4,6,9,14,15]. Prior removal of Fe(III) by extraction was found to be necessary [23].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS shows a characteristic mass of 7 pg (DL *ca* 0.02 ng ml^{-1}) for the platform atomization using a pyrocoated tube at the recommended 240.7 nm line. In ZGF AAS the 240.7 nm and the 242.5 nm lines are equally sensitive, the latter shows twice as large linearity range. Addition of HNO₃ is often sufficient [24] but the most common matrix modifier is Mg(NO₃)₂ [25,26]. Palladium increases the thermal stability of Co and allows the use of a higher ashing temperature, the addition of ascorbic acid did not improve the results [27]. The mechanism of atomization of Co from a graphite furnace has been investigated in detail [28]. Addition of H₂ to the Ar purge gas improved the peak shape, height and reproducibility, reduced the noise and resulted in a prolonged tube lifetime [29]. Solid sampling GF AAS using an inner miniature cup offered a DL of $0.15 \mu\text{g g}^{-1}$ [30]. Direct introduction of extracts into the furnace as aerosol resulted in a DL of $0.02 \mu\text{g g}^{-1}$ for environmental samples [31]. Silicate matrix was eliminated *in situ* by using an NH₄F modifier [32]. Direct GF AAS analysis of zirconium fluoride has been developed [33].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of *ca.* 5–10 ng ml⁻¹ at the most sensitive 228.62, 230.79, 236.38, 237.86 and 238.89 nm lines. The lines 236.38 and 238.89 nm are interfered with by Fe whereas the 230.79-nm line is interfered with by Ni and the 237.86-nm line by Al. Nickel overlaps at the 228.62-nm line but this interference can be corrected by the interfering element correction method. Preliminary separation of Ni from the matrix is recommended [21].

Atomic fluorescence spectrometry

Atomic fluorescence spectrometry with ETV and laser excitation offers a DL in the low pg/ml range for aqueous solutions [34]. It is degraded by an order of magnitude by solid sampling probably because

of vapour-phase interferences, losses of Co compounds during the ashing stages and quenching of the Co fluorescence [34]. The DL was *ca* 100 times poorer under vacuum conditions (0.2 ng ml^{-1}) but matrix interferences were eliminated to a large degree [35].

Mass spectrometry

Cobalt has only one stable isotope (^{59}Co) and hence TI MS is not applicable to its determination. Inductively coupled plasma MS is plagued by many polyatomic interferences, e.g. $^{40}\text{Ar}^{18}\text{OH}$, $^{42}\text{Ca}^{17}\text{O}$, $^{40}\text{Ca}^{18}\text{OH}$ [36,37].

Neutron activation analysis

The irradiation of ^{59}Co with thermal neutrons yields the metastable $^{60\text{m}}\text{Co}$ ($t_{1/2} = 10.5 \text{ min}$, $E_{\gamma} = 0.059 \text{ MeV}$) and the long-lived ^{60}Co ($t_{1/2} = 5.3 \text{ y}$, $E_{\gamma} = 1.17 \text{ and } 1.33 \text{ MeV}$). The latter nuclide is usually counted. A radiochemical separation should be performed because of interference from ^{59}Fe in the γ -ray spectrometric measurement [1,16,20,38]. A definitive method for the determination of trace amounts of Co in biological materials by RNAA has been developed [39].

24.3 ANALYSIS OF REAL SAMPLES

Cobalt is usually determined in a multielement array in a variety of environmental, geological and industrial materials (*cf.* elsewhere in Part II). Customized procedures are developed for environmental waters and biological tissues because of low concentrations present and the importance of accurate analysis, especially of clinical samples. Environmental chemistry of Co has been reviewed [40].

Water

In uncontaminated fresh waters the Co concentrations vary from 0.1 to $10 \mu\text{g l}^{-1}$ whereas in the open ocean a value of *ca* 3 ng l^{-1} is most likely. Under both fresh water and saline conditions Co^{2+} normally predominates, but in certain circumstances anthropogenic Co(III) picolinate, and to lesser extent, naturally occurring cobalamine may also be present [41]. A procedure for speciation of Co(II) and Co(III) radionuclide species has been proposed [41]. Preconcentration of Co prior to the analysis is always required. Analytical methods for the determination of total Co in water are summarized in Table 24.1.

TABLE 24.1

Determination of Co in water samples

Water (amount)	Separation/preconcentration	Detection	DL (ng/l)	Ref.
CRM sea (5 ml)	sorption of the bis(carboxy-methyl)dithiocarbamate Co complex, elution with NH_4OH	ICP MS	9	18
CRMs sea, river	sorption on algae	slurry GF AAS	n.g.	42
CRMs sea, estuarine	sorption as the DDTC complex on C_{18} column, elution with EtOH	GF AAS	1.7	19
CRMs sea, ocean (0.4–1 ml)	sorption as the DDTC complex on C_{18} resin	ETV LE AFS	1.0	43
Sea	sorption on immobilized 8-hydroxyquinoline, elution with dil. HCl	CL	0.5	13
River (5 l)	sorption on nitroso-R salt functional resin (pH 8), elution with a Ti(III) soln.	GF AAS	n.g.	12
Mineral (1 l)	anion exchange as thiocyanate complex, elution with 2 M HClO_4 -1 M HCl	ICP AES	20	21
Tap, river (0.4 l)	copptn. with Mg-oxinate	GF AAS	2.4	8
Reactor coolant (1 l)	extrn. with 2-nitroso-1-naphthol (xylene)	GF AAS	2	3
Simulated reactor coolant	extrn. with liquid surfactant membranes	GF AAS	10	44

Biological samples

The very low concentrations of Co in blood and plasma (*ca* $0.1 \mu\text{g l}^{-1}$) make it essential to take stringent precautions to eliminate contamination at all stages of the analytical procedure [27]. Several procedures have been reviewed and sources of contamination in clinical analysis have been identified [27]. Deproteinization of whole blood was found to entail the coprecipitation of Co traces with the proteins or formation of

TABLE 24.2

Analytical procedures for the determination of Co in biological materials

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL (ng/g)	Ref.
Urine	none	extrn. with N,N-hexahydroazepinium hexahydroazepine-1-carbodithioate (isopropyl ketone-xylene)	GF AAS	0.2 ^a	45
CRM urine	none	sorption of the bis(carboxymethyl)dithiocarbamate Co complex, elution with ammonia	ICP MS	0.01 ^a	18
Human tissue	aqua regia-HClO ₄	extrn. with 1-nitroso-2-naphthol (CHCl ₃)	RNAA	n.g.	1
Plant (5–10 g)	dry ashing, dissoln. in HNO ₃	extrn. with 2-nitroso-1-naphthol (heptan-2-one)	GF AAS	1	2
CRM plant (0.1–0.2 g)	HNO ₃ -HClO ₄	sorption on alumina loaded with nitroso-R-salt, elution with NaOH	FAAS	0.4	14
Fish (flesh 40 g, bone 5 g)	HNO ₃ , H ₂ O ₂	extrn. with APDC (MIBK)	GF AAS	n.g.	5
Animal and plant tissues	HNO ₃ -HClO ₄ -V(V) salt	removal of Si by evaporation with HF, anion exchange, sorption on TOPO loaded resin	RNAA	n.g.	16
Food (10 g)	HNO ₃	removal of Fe by extrn. with cupferron (CHCl ₃); extrn. of Co with APDC (MIBK)	FAAS	4	4,6
CRMs	HNO ₃ , H ₂ O ₂	anion exchange	RNAA	n.g.	20
CRMs (0.1–0.5 g)	dry ashing	none	GF AAS	n.g.	46

^a In the solution fed, ng/ml.

the stable metal bindings during the applied incubation [45]. Cobalt can be determined in plasma and urine directly by GF AAS with a DL down to 0.1 ng ml^{-1} [24,25,27] using D_2 [27] or Zeeman [24–26] background correction. Determination of Co in 5-fold diluted human serum by ICP MS has been reported [36,37]. Determination of Co in foodstuffs by FAAS and GF AAS has been compared [23]. Analytical procedures for the determination of Co in biological samples involving a separation–preconcentration step are summarized in Table 24.2.

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Copper

Copper (Cu, atomic weight 63.54, melting point 1083°C , $d = 8.93\text{ g cm}^{-3}$) is a reddish, fairly soft, ductile metal. It occurs in the earth's crust with an average abundance of 50–90 ppm, primarily as sulphide and oxide. The metal dissolves in dilute and concentrated HNO_3 , in hot concentrated H_2SO_4 , in concentrated cyanide solution [with formation of $\text{Cu}(\text{CN})_2^-$] and in NH_3aq in the presence of air [with formation of $\text{Cu}(\text{NH}_3)_4^{2+}$]. Copper exists at the II oxidation state, and, less often as Cu(I). Hydrated Cu(II) salts are blue or green in colour. Cupric hydroxide, $\text{Cu}(\text{OH})_2$, begins to precipitate at $\text{pH} \sim 5$; it shows no amphoteric properties but dissolves in NH_3aq . Copper(II) forms ammino, tartrate and EDTA complexes. Copper(I) forms sparingly soluble compounds with halogenides and soluble cyanide, chloride and ammino complexes. The demand for trace analysis for Cu arises primarily in environmental and biological sciences since Cu, although essential to life, is toxic at higher concentrations.

25.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of the Cu dithizonate (usually prior to spectrophotometry, discussed below) or the Cu dithiocarbamates is the most popular. Copper is extracted at $\text{pH} 9\text{--}11$ as the DDTC complex with CHCl_3 (also in the FI mode) [1] or over a wide range of acidities with APDC into MIBK [2–4] or DIBK [5]. Several metals are co-extracted but the virtual specificity of the method can be achieved by a careful choice of the DDTC salt used and masking [1]. Extraction of the CuI_2^- or the $\text{Cu}(\text{SCN})_2^-$ [6] complex into MIBK [7] or as an ion pair with high molecular weight amines, e.g.

TOA [8], or cationic surfactants, e.g. Zephiramine [9], usually along with Cd and Pb, is used alternatively.

Coprecipitation

Copper can be conveniently separated as CuS from acidic or neutral media in the presence of Hg, Cd, Pd or Zn as collectors. Traces of Cu can be isolated as Cu(OH)₂ with Fe(III) or Hf [10] as collectors or as sparingly soluble chelates with organic reagents, e.g. 8-hydroxyquinoline [11] or rubenic acid [12]. Electrodeposition of Cu traces is popular; an *on-line* ASV flow cell has been developed [13,14].

Sorption

Conventional anion and cation exchangers are seldom used for pre-concentration of Cu [15]; the preference being given to chelating resins. Sorption on inert supports that have been modified or loaded, e.g. with 3-aminopropyltriethoxysilane [16], 8-hydroxyquinoline [17–19], LIX 70 [20], Pyrocatechol Violet [21], has been reported, often in FI mode [18,19,21]. Copper has also been selectively retained on keratine gel [22] or by algae [23]. Ion pairs of Cu(I) cationic complexes, e.g. with 1,10-phenanthroline and tetraphenylborate were adsorbed on micro-crystalline naphthalene [24,25]. *On-line* preconcentration of the Cu-APDC complex on a C₁₈ column is gaining popularity [26].

25.2 DETERMINATION

Spectrophotometry

There are numerous organic reagents for Cu but practical significance is (and will remain) restricted only to the dithizone and DDTC methods. In acid medium (pH 1) Cu is quantitatively extracted with dithizone into CCl₄ or CHCl₃ ($\epsilon = 4.52 \times 10^4$ at 550 nm). Co-extraction of Ag is prevented with chloride. Noble metals (Pt, Pd, Au) and Hg which are co-extracted can be stripped with a KI solution. Alternatively, they can be removed prior to the extraction of Cu by shaking from 1 M mineral acid solution making use of the kinetic inertness of the Cu dithizonate formation. The dithiocarbamate method is based on the formation of the Cu-DDTC complex at pH 4–11 ($\epsilon = 1.4 \times 10^4$ at 436 nm). In optimized conditions only Bi interferes but it can be stripped with 5 M HCl [1].

Chemiluminescence

Chemiluminescence determination based on the reaction of the Cu(I)–1,10-phenanthroline chelate with H_2O_2 at alkaline pH is sensitive (DL 3 pg ml^{-1} for a $200\text{-}\mu\text{l}$ sample) and fairly selective [27].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.08 \text{ }\mu\text{g ml}^{-1}$ at the most sensitive 324.8 nm line in the recommended air– C_2H_2 flame (oxidizing, lean, blue). The sensitivity is commonly increased by extraction of Cu into an organic solvent and feeding the extract into the flame [3,4,7,8,28]. A further increase in sensitivity (DL of 0.5 ng ml^{-1}) was achieved by the use of the atom-trapping technique for APDC extracts [2]. Flame AAS with discrete nebulization of the extracts and Zeeman background correction has been studied in detail [7,28,29].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS shows a characteristic mass of 4 pg at the 324.8 nm line. Pyrocoated tubes are recommended for the avoidance of carbide formation [30]. The high atomization temperature of Cu ($2700\text{--}3000^\circ\text{C}$) allows selective volatilization of the matrix in the ashing step [30]. Copper is typically determined without a modifier because it is thermally stable to about 1100°C [31]. The allowable ashing temperature can be even higher in the presence of sulphate or nitrate owing to the stabilizing effect of oxides and sulphides [32]. With the Pd–Mg modifier the pyrolysis temperature for Cu could be increased to 1300°C [31]. Spectral interference from the Pd modifier was observed on the 324.7 nm Cu line when D_2 background correction was used [33]. This interference can be circumvented either by using the 327.4 nm line or by the use of Zeeman background correction, in both cases at the expense of a 2-fold decrease of sensitivity [31]. The relatively uncomplicated atomization of Cu makes solid sampling [11,34–38] and slurry sampling [23,37,39] GF AAS popular, especially for the analysis of environmental and biological samples.

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers DLs of $1\text{--}5 \text{ ng ml}^{-1}$ at the most sensitive 224.70, 324.75, 327.40 nm lines [39]. The 224.70 nm line is to be avoided in the presence of high levels of Fe and Pb. The 324.75 nm line should not be used for matrices containing high levels of Fe. High V concentrations cause an elevated background at 327.40 nm which can

be eliminated by background correction. The choice of emission line in the presence of the Zr matrix has been discussed [40]. Lithium solution was added to suppress ionization of Cu [41]. Internal standardization was reported to correct for mineral acid suppression [42]. Direct sample insertion into the ICP [43,44], LA for the DCP [45] and ETV for the MIP [46] were reported.

Mass spectrometry

Copper has two stable isotopes: ^{63}Cu (69.17%) and ^{65}Cu (30.82%). Thermal ionization of Cu was attained at a low temperature of 900°C despite the high ionization potential of Cu [47]. In ICP MS the ^{63}Cu nuclide is overlapped with $^{40}\text{Ar}^{23}\text{Na}$ and PO^+ , whereas the polyatomic species interfering at mass 65 ($^{33}\text{S}^{16}\text{O}^{16}\text{O}$, $^{32}\text{S}^{33}\text{S}$, $^{32}\text{S}^{16}\text{O}^{17}\text{O}$) do not constitute a major problem [48–50]. Various separation techniques, e.g. SEC [48], *on-line* ASV [13,14] and anion exchange [51], have been used to remove the spectral overlaps. Isotope dilution ICP MS employing the ^{65}Cu as the spike [52] was reported.

Neutron activation analysis

Copper may be determined using either the $^{63}\text{Cu}(\text{n},\gamma)^{64}\text{Cu}$ or the $^{65}\text{Cu}(\text{n},\gamma)^{66}\text{Cu}$ reaction [20]. Both short-lived ^{66}Cu ($t_{1/2} = 5.15$ min, $E_\gamma = 1.04$ MeV) and long-lived ^{64}Cu (β^+ emitter, $t_{1/2} = 12.8$ h, $E = 0.511$ keV) are employed for analysis. In the latter case the annihilation peak is measured with a γ -spectrometer. A radiochemical separation is required when other positron emitters are present in the sample. The formation of ^{64}Cu in the reaction $^{64}\text{Zn}(\text{n},\gamma)^{64}\text{Cu}$ interferes.

25.3 ANALYSIS OF REAL SAMPLES

Copper levels in geological and many other samples are readily determined by FAAS by feeding the solution obtained after sample decomposition to the nebulizer either directly or after extraction with MIBK (*cf.* Part II). Copper is usually included in the multielement array during characterization of industrial materials for trace elements; relevant methods can be found in Chapters 11 and 12.

Water

Direct methods, usually GF AAS, are preferred to avoid the possibility that the non-reactive Cu forms escape the analysis. The determina-

tion is interfered by with NaCl , Na_2SO_4 and NaNO_3 and CaCl_2 which are readily removed by *in-situ* thermal volatilization [32,53]. A model explaining variations of Cu signals in seawater was proposed [54]. If preconcentration procedures are used, care must be taken to release the Cu complexed by strong organic ligands, e.g. by acidification to pH 2 for a long period and UV cleavage; otherwise organically bound Cu may escape the analysis [17,27]. Direct atomization of a Cu-loaded cation exchange resin bead for the determination of Cu in tap and distilled water ($>2 \text{ pg ml}^{-1}$) has been reported [15]. Direct atomization Zeeman GF AAS for Cu in water-borne suspended matter collected on filters has been proposed; calibration was achieved with aqueous standards [55]. Analytical methods that have been claimed to determine the total Cu in water are summarized in Table 25.1.

Clinical samples

Copper in serum or plasma is largely bound to the high molecular weight proteins [48]. The normal Cu level in serum (*ca* $1 \text{ } \mu\text{g ml}^{-1}$) can be readily determined by many methods, usually by GF AAS. The preheated tube GF AAS reduces the analysis time [56]. Determination of Cu in serum by ICP AES required 10-fold dilution with water; calibration with aqueous standards was possible [57]. Accurate results were obtained in serum analysis by DCP AES if matrix-matched standards were used [57]. The direct measurement of the $^{63}\text{Cu}/^{65}\text{Cu}$ ratio in blood plasma or serum by ICP MS is precluded by the polyatomic interferences at mass 63. Determination at mass 65 [49,50] or preseparation of Cu have been proposed [14,48,51]. Saliva [58,59], whole blood [60], infant formula [61] and the haemodialysis fluid [62] can be analyzed directly by GF AAS with D_2 or Zeeman background correction down to sub-ng ml^{-1} levels. A FI FAAS system after *on-line* microwave-assisted digestion (with HNO_3 -HCl) of blood and addition of Triton X-100 was described [63]. Direct GF AAS of urine using HNO_3 as matrix modifier and Zeeman correction offered a DL of 0.75 ng ml^{-1} . An ashing step to reduce the carbon build-up in the tube and matrix-matched standards were required [60]. Copper has been determined in 10-fold diluted urine by Zeeman flame AAS with a DL of 5 ng ml^{-1} [64].

Plant and animal tissues

Solid sampling and slurry AAS have been widely used for aquatic and terrestrial plant and low animal tissues [17,33,39]. Copper can be determined directly in the acid digest (leachate) by FAAS in animal

TABLE 25.1

Determination of total copper in water

Water (amount)	Preconcentration	Detection technique	DL ($\mu\text{g/l}$)	Ref.
Tap, sea (1 l)	sorption on silica gel modified with 3-aminopropyltriethoxysilane, elution with 2 M HCl	FAAS	100	16
Sea (4 ml)	sorption on immobilized 8-hydroxyquinoline, elution with 1 M HCl	CL	0.025	17
Sea (0.2–2 ml)	sorption of Cu-APDC complex on a C_{18} column	GF AAS	0.007	26
River (0.1–0.4 l)	copptn. with $\text{Hf}(\text{OH})_4$, dissoln. in HNO_3	GF AAS	0.04	10
Not specified	extrn. as ion pair of CuI_2 with Zephiramine (DIBK)	GF AAS	2.6	9
Tap, distilled (50 ml)	cation exchange	GF AAS	0.002 ^a	15
Natural (50 ml)	extrn. with APDC (MIBK)	FAAS	0.5	2
River, hot spring (0.3–0.5 l)	sorption of ion pair of the Cu(I)-1,10-phenanthroline complex and BPh_4^- on naphthalene, dissoln. in DMF	FAAS	93 ^a	25
Tap, well, river (0.9 l)	sorption on Pyrocatechol Violet loaded Amberlite, elution with 2 M HNO_3	FAAS	n.g.	21
river (40 ml)	sorption on kerateine gel, elution with 3 M HCl	FAAS	n.g.	22
CRMs river (10 ml), sea (100 ml)	sorption on algae	slurry GF AAS	n.g.	23
Tap, river (40–100 ml)	copptn. with 8-hydroxyquinoline with Mg carrier	GF AAS	0.01	11

^a Sensitivity.

issue with a DL of $3 \mu\text{g g}^{-1}$ [65–68]. Microwave digestion is gaining popularity [69]. Copper in oils and fats can be determined directly [70,71] or on sonication with HNO_3 [72]. Milk powder is analyzed by GF AAS as slurry or by solid sampling using a $\text{Mg}(\text{NO}_3)_2\text{--NH}_4\text{H}_2\text{PO}_4\text{--Triton X-100}$ matrix modifier with a DL of 20 ng g^{-1} [37]. Milk powder was analyzed after probe atomization using aqueous standard calibration curve [73]. A rapid furnace programme GF AAS has been used for plant tissues [74]; the problem of matrix interferences was solved by dilution [74]. Lower concentrations are determined after digestion and a preconcentration step usually by FAAS and are summarized in Table 25.2.

Accuracy

The fairly high Cu concentrations commonly found and the high sensitivity of FAAS have assured a reasonable standard of the results published. Serious errors may result from the uncertain Cu speciation especially if combined procedures are used. Comparison of standard materials for the calibration of solid sampling GF AAS determination of Cu in biological samples has been presented [38]. Magnesium oxinate containing copper has been recommended for calibration; the role of Mg as a matrix modifier for direct determination of Cu has been emphasized [38]. Results of interlaboratory intercomparisons on the direct determination of Cu in oils and fats by GF AAS [76], ID ICP MS (spiked with ^{65}Cu), determination of Cu in biological reference materials after digestion with HNO_3 and HCl [52], and determination of Cu in timber treated with preservative [77] have been presented. A large number of CRMs with the certified Cu content exist (*cf.* Part II) but not for speciation analysis.

25.4 SPECIATION

There is an increasing interest in speciation of Cu in environmental and biological materials since organic complexation has a marked effect on Cu bioavailability. The relevant methods are summarized in Table 25.3.

In natural waters Cu exists in a variety of dissolved and particulate chemical forms. The dissolved forms include the hydrated Cu^{2+} cation, complexes with inorganic ligands (e.g., CO_3^{2-} , OH^- , Cl^-) and complexes with various naturally present (terrestrial humic substances, phytoplankton metabolites) and anthropogenic (EDTA, NTA) ligands [27,

TABLE 25.2

Determination of copper in biological samples

Sample (amount)	Pretreatment	Separation/pre- concentration	Detection	DL ($\mu\text{g/g}$)	Ref.
CRM urine (1 ml)	dilution with HNO_3	on-line ASV	ICP MS	0.03^a	16
Urine	acidification with CH_3COOH	extrn. of CuI_2^- with TOA (<i>n</i> -butyl acetate)	FAAS	3^a	8
Human hair (10 g)	$\text{HNO}_3\text{--HClO}_4$	sorption of ion pair of the Cu(I) – 1,10-phen complex with BPh_4^- on naphthalene, dissoln. in DMF	FAAS	93^a	25
Beverages (0.1 l)	acid	sorption of ion pair of the Cu(I) – 1,10-phen complex with BPh_4^- on naphthalene, dissoln. in DMF	FAAS	93^a	25
BioCRMs	HNO_3 (bomb)	extrn. of CuI_2^- with Zephiramine (DIBK)	GF AAS	2.6^a	9
Wood (0.4– 1.2 g)	$\text{HNO}_3\text{--H}_2\text{O}_2$ (microwave assisted)	none	FAAS	1.5	75
CRM (0.3 g)	$\text{HNO}_3\text{--HCl--}$ $\text{HClO}_4\text{--HF}$ (bomb)	extrn. with dithizone (CCl_4)	FAAS	49^a	28
Foods (1–3 g)	HNO_3 , H_2SO_4 , $\text{HNO}_3\text{--HClO}_4$ (bomb)	extrn. of CuI_2^- (MIBK)	FAAS	0.02	6
Biotissue (0.1 g)	$\text{HClO}_4\text{--HNO}_3$	extrn. chromato- graphy on LIX70	RNAA	0.015	18

^a In the solution fed, ng/ml.

TABLE 25.3

Analytical techniques for speciation of copper

Species determined	Sample	Chromatographic separation	Detection technique	Ref.
Cu-porphyrins	coals oil shale	gas chromatography	ICP MS	78
Cu cyclohexane-butyrates, Cu tetramethylheptanedionate, CuDMD	jet fuel	ion-interaction chromatography	FAAS	79
CuDMD, Cu carboxylates	jet fuel	reversed-phase chromatography	FAAS	80
Cu-thioneins	crab tissue	reversed-phase chromatography	UV	81
⁶⁴ Cu-thioneins	rat hepatoma tissue culture	reversed-phase chromatography	β-spec	82
Cu-thioneins	rat and bovine fetal liver	reversed-phase chromatography	FAAS	83
Cu-proteins	soy bean flour extracts	electrophoresis gel chromatography	FAAS	84
Cu-thioneins	mussels	size-exclusion chromatography	ICP AES	85
Cu-thioneins	cyanobacterium	size-exclusion chromatography	ICP MS	86, 87
Cu-thioneins	proteins	size-exclusion chromatography	ICP MS	88
Cu-thioneins	mussels	size-exclusion chromatography	UV	89
Cu-proteins	human serum, milk serum, seminal fluid	size-exclusion chromatography	ICP AES	90
Cu-proteins	rat blood serum, red blood cell hemolysate	size-exclusion chromatography	ICP MS	91
Macromolecular biocomplexes	natural waters	size-exclusion chromatography	GF AAS, ICP AES	92
Macromolecular complexes	humus soils	size-exclusion chromatography	ICP MS	93
Metabolites of auranofin	leachates	anion exchange chromatography	ICP MS	94
Cu bound to humic and fulvic acids	urine	size-exclusion chromatography	ICP MS	94
	sewage sludge, treated soil	size-exclusion chromatography	GF AAS	95

CuDMD = copper N,N'-disalicylidene-1,2-propylenediamine.

96,97]. Copper is largely (>99%) complexed by natural organic ligands in shelf, estuarine and open seawater samples [27]. In open ocean the dissolved Cu concentration ranges from 3 to 400 ng l⁻¹ out of which only 0.6 ng l⁻¹ is free Cu²⁺ [17]. Copper speciation has been studied by a multi-method approach including chelating resin partitioning followed by GF AAS determination [96]. Several methods for Cu speciation in marine waters by competitive ligand equilibration/liquid-liquid extraction followed by spectrometric determination have been evaluated [98, 99]. Strong acidic cation exchange and chelating resin Chelex-100 have been used for selective retention of Cu cations and readily dissociable Cu complexes [100,101]. Copper anionic complexes with humic and fulvic acids were sorbed on weak basic anion exchangers [97,101,102]. If trace cation exchange sites are saturated e.g. with In, inorganic cations and anions, EDTA complexes and colloidal hydrated Fe(III) have been reported not to be retained on Amberlite XAD-2 [97]. Macromolecular Cu complexes in natural waters have been separated by SEC prior to GF AAS or ICP AES determination [92].

Copper in soils is bound to humic substances (fulvic and humic acids) and lower relative molecular mass ligands (e.g. citric acid). Fulvic acids have generally lower relative mass than humic acids. Bound forms are not available to the plants. The lower relative molecular mass complexes are potentially available to a greater extent, Cu²⁺ ions, simple inorganic species and copper-citrate complexes are highly toxic. Different strategies to assess Cu mobilization in polluted river sediments have been examined [103].

In biological materials Cu is bound to metalloproteins. Their differentiation is usually achieved by reversed-phase or size-exclusion chromatography coupled with ICP AES or ICP MS (*cf.* Table 25.3).

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Gallium

Gallium (Ga, atomic weight 69.72, melting point 29.8°C, $d = 5.91 \text{ g cm}^{-3}$) is a soft silver-grey metal. It occurs in the earth's crust at an average level of 15 ppm, primarily along with Al and Zn ores. Unless very pure, the metal dissolves readily in mineral acids (with the formation of Ga^{3+} and evolution of H_2) and in alkali metal hydroxide solutions to produce gallate $\text{Ga}(\text{OH})_4^-$. Gallium exists in one stable oxidation state III. The hydroxide, $\text{Ga}(\text{OH})_3$ which precipitates at pH 4–6, is amphoteric. Gallium salts are generally water soluble except for carbonate and phosphate. Gallium forms halide, oxalate, tartrate and EDTA complexes. Apart from geochemical studies, the need for the determination of Ga traces is related to environmental concerns and to its applications in the electronics industry and in medicine.

26.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Gallium is extracted as GaCl_4^- from strong HCl media (3–8 M) with DEE or DIPE [1,2] or with CHCl_3 in the presence of *n*-octylamine [3]. The extraction is quantitative but not selective. Other recently proposed extractants have included a mixture of APDC–DDTC at pH 4–6 into CHCl_3 [4] and di-2-ethylhexylphosphoric acid into a molten C_{17} – C_{20} fatty acid mixture (pH 1–1.5) [5]. Sorption of Ga on immobilized 8-hydroxyquinoline resins [6–8] or Chelex-100 [7] is popular. Trace amounts of Ga can be separated by anion exchange [9,10]. Significant isotopic fractionation of Ga was observed during elution from an anion-exchange resin in the thiocyanate form [11]. Coprecipitation of Ga as hydroxide using Al, Fe(III) and Hf collectors is often used.

Spectrophotometry and fluorimetry

The most popular methods are based on the extraction of ion-associates of the GaCl_4^- complex with basic dyes (usually Rhodamine B) into a mixture of chlorobenzene and CCl_4 . The sensitivity is high ($\epsilon \approx 10^5$) but the selectivity needs to be improved, e.g. by the reduction of the interfering Fe(III), Au(III), Sb(V) and Tl(III) to their lower oxidation states. In the presence of larger quantities of these metals a prior separation of Ga (e.g. by extraction from 7–8 M HCl) is required. Fluorimetric methods based on the Ga complex with salicylaldehyde thiocarbohydrazone are sufficiently selective in the presence of fluoride and thiosulphate to be applied to a variety of real samples [12,13].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $1 \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame at the most sensitive 287.4 nm line. The alternative 294.4 nm line is a doublet (294.36/294.43 nm). Ionization should be controlled by the addition of an alkali salt (e.g. 0.1% KCl). D_2 -background correction is recommended [14].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS is prone to losses as a result of the formation of volatile oxides (Ga_2O and GaO) in consequence of the reduction of Ga_2O_3 by graphite [15] and volatile halides: GaCl [16] and GaF [11]. Equilibria of Ga_2O in the GF have been discussed; losses of Ga below 1000 K are common [15]. The matrix modifiers applied included $\text{Ni}(\text{NO}_3)_2$ [17–21], $\text{Ni}(\text{NO}_3)_2\text{-Al}(\text{NO}_3)_3\text{-EDTA}$ [22], Pd-Mg [23], $\text{Mg}(\text{NO}_3)_2$ [24] and ascorbic acid [25]. A mixture of $\text{HNO}_3\text{-H}_2\text{SO}_4$ [16,26] and $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ [16] promote the formation of Ga_2O_3 of higher thermal stability. Alumina was reported to decrease volatility of Ga and thus to increase sensitivity of the determination by a factor of 8 [27]. Sensitivity enhancements are generally more pronounced in pyrolytically coated furnaces [25]. When Ga is to be determined in organic matrices (that yield free carbon during pyrolysis), matrix matching of samples and standards is mandatory [25]. The spectral overlapping of the 287.424 nm Ga line by Fe (287.417 nm) gives rise to overcorrection errors with D_2 background correction [26,28]. A secondary line (294.42 nm) has been used to avoid Fe interference [24,26]. A combination of Zeeman correction and L'vov platform atomization was recommended [17,24–26].

Inductively coupled plasma techniques

ICP AES offers a DL of 30–50 ng ml^{-1} at the most sensitive 294.36 nm

line [29]. The other lines (287.424 nm and 417.190 nm) are interfered with by V (287.420 nm) and Fe (287.417 and 287.430 nm) and Mo (417.190 nm). Gallium has two natural isotopes: ^{69}Ga (60.08%) and ^{71}Ga (39.92%). Isotope dilution ICP MS analysis has been developed [1].

Neutron activation analysis

Gallium is usually determined by γ -counting of the ^{72}Ga ($t_{1/2} = 14.2$ h, $E_{\gamma} = 0.63$ and 0.834 MeV). Short-lived ^{70}Ga ($t_{1/2} = 21$ min) formed by the (n,γ) reaction from ^{69}Ga is of less significance. For INAA Ga should be separated from Fe to avoid $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ (0.835 MeV) which would interfere with ^{72}Ga (0.834 MeV) [30]. Radiochemical separation was found to be necessary to match the Ga levels in natural water and biological samples [4].

26.2 ANALYSIS OF REAL SAMPLES

Methods for the determination of Ga in water are summarized in Table 26.1. The typical concentration in natural waters is *ca* 10 ng l $^{-1}$ and a preconcentration step is required. Open ocean water contains 0.15–2 ng l $^{-1}$ Ga and needs to be processed in a class 100 environment [7]. Blanks from immobilized 8-hydroxyquinoline resin of below 0.2 ng l $^{-1}$ have been reported [8]. For solid samples digestions with HCl [16], HClO $_4$ [17] and HF [11] introduced in the sample decomposition step increase the risk of volatility losses in GF AAS.

Gallium in rocks and ores is usually determined directly after acid decomposition by GF AAS [17,19,20,24]. For the determination of Ga in industrial process wastes FAAS [14] and ICP AES [29] are the methods of choice. Gallium was determined accurately in aluminium after extraction as GaCl_4^- (DIPE) and back-extraction into water by ID ICP MS [1]. Slurry atomization GF AAS has been proposed for the determination of Ga in alumina [9] and coal and coal fly ash [21]. Gallium has been determined in Ni alloys by GF AAS after acid decomposition of the sample [26].

Analysis of soft animal tissues and urine after digestion with HNO $_3$ –H $_2$ O $_2$ using fluorescence techniques was reported to offer DLs of 1.5– 2 ng ml $^{-1}$ in the solution fed [12,13]. Gallium was determined in plants by GF AAS directly after acid digestion [17] and by NAA after extraction with APDC–DDTC [4] or cation exchange [30] with ADLs down to 1 ng.

TABLE 26.1

Methods for the determination of Ga in waters

Water (amount)	Separation and/or preconcentration	Determination technique	DL (ng/ml)	Ref.
Natural (0.4 l)	extrn. with APDC-DDTC (CHCl_3), stripping with $\text{Pb}(\text{NO}_3)_2$ soln.	NAA	0.001	4
Sea (2 l)	sorption on Chelex-100, elution with 2.5 M HNO_3 , evaporation	GF AAS	0.1	7
Sea (10 l)	sorption on 8-hydroxyquinoline resin, elution with 2.4 M HNO_3	GF AAS	0.1	7
Subsurface sea, river (0.25–0.5 l)	sorption on 8-hydroxyquinoline resin, elution with HNO_3 –HCl	GF AAS	0.25	8
Sea, lake (10 l)	anion exchange	VIS		10
Waste, drinking, mineral	none	DSF	1.5	13
River, sea (0.05–0.4 l)	copptn. with $\text{Hf}(\text{OH})_4$, dissoln. in HNO_3	GF AAS	0.1	31
Waste	extrn. with HDEHP (molten C_{17} – C_{20} fatty acids)	XRF	500	5
Waste	sorption on a phosphoramidate chelating fibre, elution with HCl	ICP AES	n.g.	32

DSF = derivative synchronous fluorescence.

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Germanium

Germanium (atomic weight 72.59, melting point 927°C, $d = 5.32 \text{ g cm}^{-3}$) is a hard, greyish-white metalloid. It occurs in the earth's crust with the average abundance of *ca* 7 ppm, mostly along with Pb–Zn–Cu ores but it is also abundant in coal. Germanium dissolves in concentrated HNO_3 or H_2SO_4 to form GeO_2 , and in *aqua regia* to produce GeCl_4 . It is attacked by peroxides, fused alkalis, nitrates and carbonates with the formation of germanate. The typical oxidation states of Ge are IV and –IV (in the hydride). Germanium dioxide (GeO_2) is sparingly soluble in water with formation of germanic acid (H_2GeO_3). Both GeCl_4 (a volatile liquid) and GeF_4 (a gas) are readily hydrolyzed. Germanium(IV) forms halide and oxalate complexes and heteropoly acids. Hydrogen sulphide precipitates GeS_2 from strongly acid media which dissolves in alkalis. The analytical chemistry of Ge has been discussed [1].

27.1 SEPARATION AND PRECONCENTRATION

Volatilization

Germanium hydride (GeH_4 , germane) is formed in the reaction of Ge with NaBH_4 at pH 4–5 (acetic buffer) [2,3], and at pH 6.5 (phosphate buffer) [4] or in a HNO_3 –citrate medium [5]. A Tris–HCl buffer [6] or a malic acid medium [7] have been recommended for the generation of methylgermanium [$\text{Me}_{3-n}\text{Ge}^{n+}$ ($n = 0, 1, 2$)] hydrides. Many ions (especially transition metals) interfere severely and should be masked, e.g. with EDTA [6,7], L-cysteine [8,9] or thiourea [8,10]. In particular, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used to suppress interferences from Al, As, Cu, Hg, Pb and Sn [10] whereas histidine was found to be efficient in alleviating the Ni interference [8]. The hydride(s) formed can be trapped cryogeni-

cally and then thermally released into the detector [5–7] or preconcentrated in the graphite oven by thermal decomposition [2,11,12]. Other methods for volatilization include ethylation of $\text{Me}_{3-n}\text{Ge}^{n+}$ species with NaBEt_4 [13] or distillation of GeCl_4 from HCl medium [14]

Extraction

Extraction of GeCl_4 from 9 M HCl into CCl_4 or CHCl_3 followed by back-extraction into H_2O is very selective [3]. Methyl-, ethyl- and phenylgermanium chlorides are extracted to different degrees [15]. Extraction of inorganic and methylated Ge with organic ligands containing a negatively charged oxygen donor has been exhaustively discussed [16]. Germanium has been retained as molybdo germanate (pH 0.5–3.7) on polyurethane foam [17].

Coprecipitation

Coprecipitation of traces of germanium with $\text{Mg}(\text{OH})_2$ [18] or $\text{Hf}(\text{OH})_4$ carriers (pH 9–10) [19] has been discussed.

27.2. DETERMINATION TECHNIQUES

Spectrophotometry

Germanium reacts with phenylfluorone at pH 4–5 to yield a red–orange complex ($\epsilon = 5.3 \times 10^4$ at 510 nm) [14]. Sensitivity can be improved by the use of surfactant, e.g. CTA ($\epsilon = 1.7 \times 10^5$ at 507 nm) [14,20]. Methods based on ion-associates of germanomolybdate with basic dyes floated with toluene and dissolved in methanol are very sensitive ($\epsilon = 1\text{--}6 \times 10^5$). Spectrophotometric methods are routinely preceded by extraction of GeCl_4 with CCl_4 .

Flame atomic absorption spectrometry

An $\text{N}_2\text{O}\text{--C}_2\text{H}_2$ reducing (rich, red) flame is recommended to destroy Ge oxide species formed. The recommended 265.1 nm line is actually a doublet (265.12 nm/265.16 nm). Both EDLs and HCLs are available and provide approximately the same sensitivity and detection limit. The sensitivity of QF AAS is exceptionally poor. Detection limits in the range of $0.01\text{--}0.5 \mu\text{g ml}^{-1}$ are achieved.

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 10–15 pg. The

determination is affected by losses of volatile GeO, GeS and/or GeCl₄ prior to atomization [21,22]. A pyrolysis temperature of 800 °C can be applied without a matrix modifier [21]. To increase it to 1400–1500 °C various modifiers such as NaOH [23–25], HNO₃ or HClO₄ [25], Mg(NO₃)₂ [26], Ni(NO₃)₂ and Ba(NO₃)₂ [27], Ni(NO₃)₂ and Fe(NO₃)₃ [28], Co(NO₃)₂–Al(NO₃)₃ [29], Pd(NO₃)₂ and Pd(NO₃)₂–Mg(NO₃)₂ [2,16] have been proposed. The atomization mechanisms have been studied [23–25,28]; atomization from a pyrolytic graphite platform is recommended [2,26]. Impregnation of the tube surface by carbide-forming elements also leads to an enhancement of absorbance [23,25]. Chloride, bromide and especially sulphate interfere [21,25]. Sensitivity can be improved by *in-situ* preconcentration of germane in a GF modified with Pd [2,11,12]. The response for organogermanium compounds is species dependent [6].

Atomic emission spectrometry

Germane can be efficiently atomized in an H₂–air flame [5]. ICP AES offers sensitivity of 50–100 ng ml^{–1} at the most sensitive 265.12, 209.43 and 219.87 nm lines. Overlaps with Mn, Ti, Fe, U, W and REE are common for spectrometers with poor resolution [27]. Germanium and its compounds are stabilized by HF and NaOH [30]. In dilute HCl the transport efficiency, and thus sensitivity, increases *ca* 50–60 times owing to the formation of volatile chloride [30]. The introduction of GeH₄ into a plasma (ICP or DCP) is another way to improve the transport efficiency [4,9,18]. Emission enhancement in the presence of easily ionized elements in the DCP has been reported [31].

Mass spectrometry

Germanium has five naturally occurring isotopes: ⁷⁰Ge (20.52%), ⁷²Ge (27.43%), ⁷³Ge (7.76%), ⁷⁴Ge (36.53%) and ⁷⁶Ge (7.76%). The ADLs in ICP MS reach the 0.1. pg level on hydride generation [7]. The ⁷⁴Ge is usually monitored. The ⁷⁴Se nuclide (abundance 0.87%) may interfere but SeH₂ (if present) can be removed in the CO₂ trap prior to reaching the plasma.

Neutron activation analysis

This is based on counting the ⁷⁵Ge (*t*_{1/2} = 82 min) and ⁷⁷Ge (*t*_{1/2} = 12 h) nuclides. ⁶⁰Co interferes severely [5]. Radiochemical separation is necessary.

27.3 ANALYSIS OF REAL SAMPLES

A principal concern is the possibility of loss of Ge as GeCl_4 during digestion. The use of HCl or chlorides in the preparation of standards may cause volatilization losses. Fusion of rocks is discouraged not only because of loss hazards but also because of the falling out of the silica gel formed on acidification required prior to hydride generation. Up to 20–30% of Ge can be lost from biological samples during dry ashing or open-vessel wet digestion in the presence of normal biogenic levels of chlorine [14]. Decomposition with $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ in a closed system followed by distillation of GeCl_4 has been proposed [14]. In the case of geosamples the use of a $\text{H}_2\text{SO}_4\text{--HF}$ mixture creates a risk of Ge loss by coprecipitation with Ba, Ca and Sr sulphates formed [3]. A decomposition with a $\text{HF--H}_3\text{PO}_4$ mixture has been recommended; the phosphate precipitates are easily dissolved in HCl [3]. Sulphide ores should be predigested with HNO_3 to avoid loss of GeS_2 [3]. Microwave-assisted pressure digestion of ores and solid wastes with $\text{HNO}_3\text{--HF}$ has been recommended [32]. Semiconducting materials are analyzed by GF AAS directly after decomposition [27]. Methods for the determination of total Ge are summarized in Table 27.1.

The increasing interest in biomethylation of Ge requires its speciation. Methylgermanium species are usually purged as hydrides, cryotrapped on a GC sorbent and, on thermal release, determined by GF AAS [6,34,35] or ICP MS [7]. The methods have been applied to seawater [6,7,35] and fresh water [6,7,34].

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TABLE 27.1

Methods for the determination of germanium traces

Sample (amount)	Dissolution	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Sea, river, spring water (50–200 ml)	none	copptn. with $\text{Hf}(\text{OH})_4$, volatn. as GeH_4	GF AAS	0.5 ^a	19
Natural waters (1 l)	none	copptn. with $\text{Mg}(\text{OH})_2$, volatn. as GeH_4	DCP AES	0.0006 ^a	18
Spring water (10 ml)	none	sorption of the Ge– phenylfluorone complex on cellulose	VIS	50 ^b	33
CRM rocks, ores (1 g)	HNO_3 , $\text{HF-H}_3\text{PO}_4$	extrn. of GeCl_4 (CCl_4), back-extrn. (H_2O), volatn. as GeH_4	FAAS	50 ^a	3
Meteorites (0.1 g)	HNO_3 (bomb)	volatn. as GeH_4	FAAS	30	5
CRM copper (1–1.5 g)	HNO_3	volatn. as GeH_4	DCP AES	20	9
CRM iron (1–1.5 g)	<i>aqua regia</i>	volatn. as GeH_4	DCP AES	20	9
Semiconductor materials (20–40 mg)	HNO_3	volatn. as GeH_4	FI ICP AES	0.4 ^b	4
Polymers (1 g)	CH_3COOH (leaching)	volatn. as GeH_4	FI ICP AES	0.4 ^b	4

^a ng/ml in the analyzed solution; ^b absolute detection limit, ng.

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Gold

Gold (Au, atomic weight 196.97, melting point 1063°C , $d = 19.3 \text{ g cm}^{-3}$) is a noble, easily malleable, yellow lustrous metal. It occurs in the earth's crust with an average abundance of $3.5 \mu\text{g g}^{-1}$. Gold mostly occurs as native metal in lode and placer deposits often in association with quartz. Gold is also present as a minor component of base-metal ores, especially those of copper obtained as a by-product in the electrolytic refining of copper and nickel. The metal is used in electronic industry and in jewellery. Gold compounds are used in medicine because of their antitumour and antirheumatoid activity.

Gold normally resists corrosion by a single mineral acid but dissolves in *aqua regia* with formation of chloroauric acid, HAuCl_4 . Gold dissolves (at ambient temperature) in alkali cyanide solution in the presence of atmospheric oxygen to form a stable $\text{Au}(\text{CN})_2^-$ complex. It is also attacked by fused alkali containing an oxidizing agent to produce soluble aurates. The most common valence states of gold are I and III giving origin to aurous and (more stable) auric compounds, respectively. The Au(I) and Au(III) ions do not exist in aqueous solutions; analytical chemistry of Au is based on chloride and bromide complexes of Au(III). Gold(III) forms relatively stable nitrate complex which often makes it necessary to eliminate nitrate from solutions obtained on dissolving Au in *aqua regia*. The hydroxide, $\text{Au}(\text{OH})_3$, is amphoteric. When Au solutions are treated with NH_3aq an explosive fulminate may be formed. The gold in chloride solution is readily reduced to the colloidal metal by many organic (e.g. ascorbic acid, oxalic acid, hydrazine, hydroquinone) and inorganic reducing agents (e.g. Zn , SnCl_2 , H_2O_2), some of which do not precipitate the Pt-group metals. The analytical chemistry of Au has been reviewed [1–3].

28.1 SEPARATION AND PRECONCENTRATION

Extraction

Gold(III) is readily extracted from 4–8 M HCl or HBr as AuCl_4^- or AuBr_4^- , respectively, into oxygen containing organic solvents, e.g. DIPE, MIBK, ethyl or amyl acetate. The interference of Fe(III) is removed by its reduction to Fe(II) [4] or by stripping of Fe(III) with 0.5 M HCl [5]. Extraction of Au(III) halide complexes or Au(I or III) cyanide complexes as ion pairs with quaternary ammonium salts is less popular [6–8]. Trace amounts of gold can be extracted with DIPE from 7 M HNO_3 [9]; only U(VI) and Th are partly co-extracted. Although extraction of Au(III) is often claimed to be quantitative, the degree of extraction of Au from real matrices may be dependent on the composition of the solution. It is therefore recommended to match the sample matrix with standards as closely as possible.

Coprecipitation

Gold may be concentrated by precipitation on reduction to the metal, in the presence of a collector, usually Hg [10,11], Te [12–15] and mixed Se–Te [16]. Copper is used as a collector for the coprecipitation of gold as sulphide using thiourea and thioacetamide. 2-Mercaptobenzothiazole and thiobarbituric acid are common group reagents for noble metals [17]. Trace amounts of gold can be enriched by flotation using dimethylaminobenzylidenerhodanine [18], 2-phenylethylenephosphonic acid [19] or basic dyes [20,21], or by accumulation by bacterial cells [22]. Separation of Au on Nb cathode has been reported [23].

Sorption and ion exchange

Activated charcoal is the most frequently used sorbent as it retains ionic and colloidal gold quantitatively at $\text{pH} \leq 5$, is readily adaptable to field sampling and can be easily handled for NAA and AAS determinations [26,27]. Anion exchange resins which bind strongly gold(III) chloride complex are a viable approach [26–34]. Various chelating resins, polyDDTC [35], dehydrodithizone [36,37], thiol cotton fibre [38], silica gel modified with γ -aminopropyltriethoxysilane [39] and poly(vinylthiopropionamide) [40], di(methylheptyl)methyl phosphonate loaded resin [41], usually of transient importance, have been proposed. Cation exchange resins are convenient to separate base metals since Au chloride complexes are not sorbed. In contrast to charcoal, the resins allow a quantitative recovery of ionic gold whereas the retention of colloidal gold which is trapped mechanically in the resin voids is often not quantitative.

28.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometry of Au is based either on complexes with organic S-donor reagents (usually thio-Michler's ketone and rhodanine) or on ion associates of an anionic gold halide complex with basic dyes (usually Rhodamine B). Thio-Michler's ketone reduces Au(III) and forms with Au(I) colour ($\epsilon = 1-2 \times 10^5$) complexes of different composition. Rhodanine forms in a 0.1 M HCl medium a sparingly soluble pink-violet complex which remains dispersed in the aqueous phase ($\epsilon = 5.8 \times 10^4$ at 515 nm in H₂O-pyridine medium). The most popular is the ion associate of AuCl₄⁻ with Rhodamine B which is extracted with benzene or DIPE ($\epsilon = 8.7 \times 10^4$ at 565 nm). Sb(V), Tl(III), Fe(III), Ga and Hg(II) interfere and must be separated beforehand. In flotation-spectrophotometric methods an adduct of a simple ion associate of the AuBr₄⁻ complex with a basic dye and several molecules of the salt of the dye precipitates on the wall of a separating funnel during the shaking of the aqueous phase with a nonpolar solvent. The precipitate is dissolved in a polar solvent and the solution obtained is the basis for the sensitive determination of gold ($\epsilon = 11.4 \times 10^5$) [20,21]. The methods, however, lack precision unless in the hands of an experienced analyst.

Spectrofluorimetry

In spectrofluorimetric methods blue fluorescence exhibited by the extract of the ion-associate of AuCl₄⁻ (or AuBr₄⁻) with Rhodamine B or Butylrhodamine B is measured.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of 2 $\mu\text{g ml}^{-1}$ in the recommended N₂O-C₂H₂ flame at the most sensitive 242.8 nm line. A 1% solution of LaCl₃ is commonly used to control the interferences although the use of triethanolamine has been reported [42]. Flame AAS of the organic phase after extraction with MIBK is popular. Silver, Se(IV), Te(IV), Fe(III), Tl(III), Cr(VI), Mo(VI), As(V), Sb(V) and Sn(IV) are partially co-extracted but do not interfere with the measurement.

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of ca 10 pg. It is plagued by interferences which are difficult to remove by optimization of the GF programme. The maximum allowable char temperatures of

800–900°C are just below the char temperature of the carbonaceous material and the volatilization temperature of common salts such as NaCl or MgCl₂ which interfere with the formation of Au atoms. The char temperature can be increased by 300–400°C by the use of a matrix modifier, most often nickel or a Pd–Mg mixture. Interferences and matrix modifiers in ETA AAS of Au have been critically discussed [43,44]. L'vov platform atomization, Zeeman effect background correction and peak area absorbance measurements are a must for a successful analysis.

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers detection limits of 0.02 and 0.03 µg ml⁻¹ at the two most sensitive Au lines, 242.795 nm and 267.595 nm, respectively. The former is interfered by Fe, Mn whereas the latter by Fe, Cr, Mg, Mn and V. In practice the determination of Au requires separation and preconcentration [35].

Neutron activation analysis

Gold is an element with one of the best sensitivities in NAA. It is subject to the activation reaction: $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$ producing ^{198}Au nuclide ($t_{1/2} = 2.7$ d, $E_\gamma = 0.413$ MeV) which is counted, usually after a 3–10 day decay. The interferents include Ag (the $^{110\text{m}}\text{Ag}$ γ -photopeak at 0.455 MeV) and Pt, Pt (owing to the interference of the 3.15-day ^{199}Au daughter isotope) as well as ^{76}As and ^{81}Br which might be critical for the determination of Au at the ng/g level. Simultaneous determination of Au and Pt is possible but should be considered for each material and the Pt/Au ratio in the sample must be taken into account. Radiochemical NAA allows the detection limits at the low ng/g and the sub-ng/g level to be obtained for most of the samples [26,45–48].

Mass spectrometry

Gold is monoisotopic and cannot be determined reliably by TI MS. ICP MS analysis for gold offers high sensitivity (DL 0.06 ng ml⁻¹) [49,50]. The few possible isobaric interferences at mass 197 include a hydride of ^{196}Pt and ^{181}Ta oxide [51]. To date, ICP MS coupled to HPLC is the only technique capable of the speciation analysis of gold metabolites in biological samples [52].

Fluorescence techniques

The direct XRF analysis is hampered by the high content of admixtures that give energetically similar K and L series X-rays and by the strong absorption of gold X-ray fluorescence by the base elements in the

samples [53]. Gold sorbed on organic support may be analyzed [53]. Non-dispersive AFS allows a low detection limit of *ca* 0.5 ng ml⁻¹ or 0.01 μg g⁻¹ in the solid sample. Large scatter signals due mainly to Al and refractory metals make separation necessary [7]. A detection limit of 10 fg was obtained by ETV LE AFS [54].

28.3 ANALYSIS OF REAL SAMPLES

28.3.1 Geological materials

Gold is always extremely dispersed in the raw material (the nugget effect) so large sample weights are required for a representative sample. The malleability of gold makes it difficult to grind, and there may be some losses on the grinding surfaces. Samples to be analyzed should have a particle size below 200 mesh. The most common approaches to transfer gold into solution include the fire assay (*cf.* Section 2.2.3.) followed by the button dissolution or acid leaching. Alkali fusions which are used in post-irradiation decomposition of samples are considered unsuitable for other techniques unless removal of a salt matrix is included. Methods for the spectrometric analysis for Au in geological samples are summarized in Table 28.1.

The classical fire assay enables the quantitative collection of gold in the lead button which is then dissolved, usually in *aqua regia*, to produce a solution for an instrumental determination. Fire assay suffers from loss of accuracy when low levels of gold (<400 ng g⁻¹) are present. Losses of gold can be caused by boiling over and spitting during fusions, non-recovery from slag and loss into the cupels. Low recoveries can be encountered from some sample types. If the Cu, Fe or Zn content of the sample is fairly high, slag retention and cupel adsorption of Au are appreciable. The lead fire assay is inadvisable for samples containing osmiridium owing to spitting during cupellation resulting in losses of Au and the risk of contamination. Second fusion is necessary to recover gold from the silicate glass. Nickel sulphide [13,17] and copper fire assays [71] have alternatively been proposed.

The most frequently used is the halide acid leach, using *aqua regia* but a preliminary attack by Br₂ and HBr has been advocated [72]. Roasting of samples containing sulphides and organic matter at carefully optimized conditions is necessary to eliminate S and As. Below 500°C the decomposition of sulphides and some carbonaceous material

TABLE 28.1

Determination of gold in geological materials

Material (amount)	Sample decomposition	Separation technique	Detection technique	DL (ng/g)	Ref.
Ores (1–50 g)	roasting, lead fire assay, the bead dissolved in HClO_4 –AcOH	pptn. with HCHO , dissoln. in <i>aqua regia</i>	GF AAS	n.g.	17
Rocks, ores (20–50 g)	NiS fire assay; the bead dissolved in HCl	copptn. with Te	NAA	0.2	13
CRM (4 g)	dissoln. in <i>aqua regia</i> , fusion with Na_2O_2	copptn. with Te	DCP AES	n.g.	55
Sand, rocks, ores (25 g)	NiS fire assay		INAA	2	56
Rocks (10 g)	<i>aqua regia</i> (leaching)	co-pptn. with Hg, dissoln. in <i>aqua regia</i>	FAAS	n.g.	10
Rocks, ores (25 g)	<i>aqua regia</i> (leaching)	extrn. into a fraction of crude oil distillate	FAAS	18	57
Rocks (10 g)	<i>aqua regia</i> (leaching)		ICP MS	n.g.	58
Ores (25 g)	HNO_3 (leaching), roasting, dissoln. in <i>aqua regia</i>	sorption on TBP modified support	XRF	10	53
Rocks (5 g), ores (2 g)	HF – <i>aqua regia</i> (leaching); fusion with Na_2O_2	cation exchange	GF AAS	n.g.	12
Ores	H_3PO_4 – HClO_4 (leaching); HBr – Br_2	extrn. into AmAc upon redn. of Fe(III)	GF AAS	1	5
Rocks and placers	HCl – Br_2 (leaching)	copptn. with Te	AAS	n.g.	59
Rocks	<i>aqua regia</i>	extrn. into MIBK	GF AAS	0.3	60
Ores (10 g)	<i>aqua regia</i>	extrn; fibre	FI FAAS	10	61

Material (amount)	Sample decomposition	Separation technique	Detection technique	DL (ng/g)	Ref.
Ores (5–9 g)	HNO ₃ , <i>aqua regia</i>	extrn. with N, N'- diphenylbenzamidine	VIS	1000	62
Ores (0.5–1 g)	HNO ₃ –HF (bomb)	anion exchange as AuCl ₄ ⁻ , extrn. with RhB	VIS	n.g.	63
Ores		anion exchange of AuCl ₄ ⁻	WD XRF	200	64
CRMs (10 g)	HNO ₃ –HCl (microwave assisted)	sorption on Cellex T	FI FAAS	2.2 ^a	33
Rocks (10 g), ores (5 g)	<i>aqua regia</i> –Br ₂	anion exchange	FAAS	1000	28
Ores, concentrates	HF– <i>aqua regia</i>		GF AAS	100	65
Rocks (5 g)	HF– <i>aqua regia</i> (bomb)	anion exchange	GF AAS	0.5	34
Ores (~ 5 g)	HF, HNO ₃ , <i>aqua regia</i>	extrn. with amidine (CHCl ₃), back-extrn. with thiourea	AAS	600	66
Geo CRMs (0.5 g)	HCl–HNO ₃	copptn. with Hg	GF AAS	n.g.	11
Sulphide ore (25 g)	HCl, HNO ₃ , HF	sorption on activated charcoal	GF AAS	2	25
Ore (10 g)	roasting, <i>aqua regia</i>	extrn. into MIBK after pptn. of Fe(III) with NH ₃ (aq)	GF AAS	10	67
Rocks (30 g)	roasting, HCl–HNO ₃	extrn. with Aliquat-336 in DIBK	ND AFS	10	7
Rocks (5–10 g)	roasting, HBr–Br ₂	copptn. with Te	FAAS	15	14
Rocks (2–8 g)	roasting, <i>aqua regia</i>	sorption on a foamed plastic, ashing, dissoln. in <i>aqua regia</i>	Arc ES	0.3	68

continued

TABLE 28.1 (continuation)

Material (amount)	Sample decomposition	Separation technique	Detection technique	DL (ng/g)	Ref.
Ores (10 g)	roasting, <i>aqua regia</i>	<i>on-line</i> sorption	FI FAAS	50	27
Ores (2.5 g)	roasting, <i>aqua regia</i> (leaching), fusion with Na ₂ O ₂	sorption on dehydro- dithizone column, elution with thiourea	DCP AES	n.g.	36, 37
Rocks (5 g)	roasting, H ₂ SO ₄ - HF (leaching), fusion of with Na ₂ O ₂ -NaKCO ₃	copptn. with Se-Te	GF AAS	0.5	16
CRMs coal and rock	fusion with NaOH- Na ₂ O ₂	anion exchange	NAA	1 ^b	26
Rock (~0.5 g)	fusion with Na ₂ O ₂ , lead fire assay, fusion with NaOH- Na ₂ O ₂		NAA	0.008	45
Pt ore (0.5 g)	fusion with LiBO ₂ , dissoln. in HNO ₃	SPE on polyDDTC resin, dissoln. in 50% H ₂ O ₂	ICP AES	620	35
Soils	dissoln. in HNO ₃ - HCl with KBrO ₃	extrn. into MIBK	GF AAS	n.g.	69
Soil and sludge (1-2 g)	<i>aqua regia</i> (leaching), HCl- HClO ₄	sorption on thiol- cotton fibre column, leaching with <i>aqua regia</i>	ICP AES	n.g.	38
Humus soil (3 g)	leaching with <i>aqua regia</i> for strongly bound Au and dil. HCl for weakly bound Au		ICP MS	(0.2 -16)	70

SPE = solid phase extraction.

^a In the reduction fed, ng/ml; ^b ADL, pg

may be incomplete whereas above this temperature volatilization of gold may occur especially when large amounts of As and Sb are present. In addition, trapping of the gold present may occur owing to the sintering of certain clays. For some types of samples the recovery of Au can be low because of the inability of these acids to liberate gold occluded in silicates, spinels and refractory minerals. Hydrofluoric acid facilitates

release of Au grains but requires the use of expensive platinum or PTFE crucibles. Typical problems include the formation of emulsions during solvent extraction, the co-extraction of Fe(III) and losses of Au due to CO₂ evolution and frothing as the reaction with carbonates is very vigorous. Cyanide or thiourea leaching is slow and fails to liberate gold enclosed in gangue and sulphides.

28.3.2 Other materials

Water

The analysis of waters is affected by contamination and the uncertainty about gold speciation. Analytical methods for ionic gold may not be adequate for the measurement of total gold. Checking the recoveries by means of ionic standards often leads to false conclusions. In oxic seawater Au is predicted to be in the monovalent state as the neutral Au(OH)(H₂O) or AuCl₂ species but if the equilibrium is not attained soluble Au(III) complexes and Au⁰ colloids are common. Under anoxic conditions, in the presence of sulphide Au(HS)₂⁻ and Au⁰ are predicted to dominate [73]. In fresh waters dissolved organic acids (able to reduce gold to Au⁰) play an important role. Speciation of Au is further complicated by the formation of soluble auriferous humate and fulvate complexes and/or adsorption on particulate matter.

To avoid the loss of gold by adsorption on the wall of a sample container, samples should be acidified immediately after collection with HCl and some Br₂ should be added. In spite of acid additions, amorphous Si and sulphide minerals (hydrothermal fluids) rapidly precipitate and take up Au. A minimum amount of Br₂-HF-HNO₃ should be added to resolubilize the material [51]. Further, indiscriminate acid additions can promote Au losses in glass and polyethylene containers. An alternative to Br₂ addition is the adsorption of gold on charcoal just after the sample has been filtered. Because of very low concentration of Au in natural waters (in open sea 1–100 pg l⁻¹, in surface waters 0.1–1 ng l⁻¹) a preconcentration step is always required. Ion exchange resins are well suited for the determination of gold from seawater but charcoal sorption has a more universal character. The methods for the determination of Au in water are summarized in Table 28.2.

Biological materials

Dry ashing is not recommended as some plants are cyanogenic and all or part of the Au contained may be lost by volatilization. In wet digestion

TABLE 28.2

Methods for the determination of gold in water

Water (amount)	Preconcentration	Detection technique	DL (ng/ml)	Ref.
Natural (1 l)	sorption on activated charcoal, ashing, the residue dissolved in HCl	GF AAS	0.5	24
Natural (2 l)	anion exchange, elution with acetone-HNO ₃ , extrn. of AuBr ₄ ⁻ (MIBK)	GF AAS	0.4	74
Natural (2 l)	extrn. as AuCl ₄ ⁻ (MIBK)	ICP MS	0.2	74
Sea	anion exchange, upon elution resorption on a single anion exchange bead	GF AAS	<0.100	75
Ssea (4 l)	anion exchange, elution with hot concd. HNO ₃	FI ICP MS	0.002	51
Rriver, mineral (1 l)	SPE on TBP saturated with chlorine, ashing or elution with thiourea	NAA	0.2	76
Natural (1 l)	anion exchange; elution with acetone-HNO ₃ , evaporation, dissolution in HBr/Br ₂ , extrn. into MIBK	GF AAS	1	29
Sea	UV irradiation, evaporation with HF, redissoln. in <i>aqua regia</i> , anion exchange, elution with hot concd. HNO ₃	ICP MS	80	30
Lake (0.1 l)	evaporation, dissoln. in HCl-HNO ₃ , extrn. into MIBK	GF AAS	few	77

with a mixture of H₂SO₄, HClO₄ and HNO₃ plant materials may yield some insoluble white precipitates (which appear to be metal oxides) occluding gold and making the addition of HF necessary. In addition, gold complexes can be reduced readily by chemicals such as amino acids to colloidal gold, which is adsorbed on the walls of vessels. In most oxidizing media: HClO₄-HNO₃, concentrated HNO₃, fuming HNO₃ and HNO₃-H₂SO₄ incomplete recoveries are observed above 100 °C. Addition of *aqua*

TABLE 28.3

Methods for the determination of gold in biological and clinical materials

Material (amount)	Digestion	Separation	Detection technique	DL (ng/g)	Ref.
Plant (1 g)	fuming HNO_3	extrn. into MIBK from $\text{HCl}-\text{Br}_2$ medium	GF AAS	0.2	5
Plant (1–2 g ash)	dry ashing, dissoln. in <i>aqua regia</i> –HF	copptn. with Te	GF AAS, ICP MS	0.5	15
Plant, animal CRMs	HNO_3 – H_2SO_4 – HCl (HF added for plants)	pptn. as Au^0	RNAA	10 fg/g	46
Plant, animal CRMs	(??)	extrn. with DDTc	RNAA	few	47
Animal tissue (2 g)	H_2SO_4 – HClO_4 – HNO_3 , then with <i>aqua regia</i>	extrn. into MIBK	GF AAS	0.10	78
Intraocular fluid, animal tissue (<0.2 g)	HNO_3 – H_2O_2	none	GF AAS	n.g.	79
Animal serum	Triton X-100 added		GF AAS	1	80
Blood, serum	none	none	GF AAS	160 (plasma) 64 (blood)	81
Urine (25 ml)		extrn. of AuI_4^- with TOA (n-BuAc)	GF AAS	12	6
Human bone (0.1 g)	HNO_3 (microwave assisted)	extrn. into MIBK	GF AAS	40	82

regia and gentle heating over a water bath prevent losses [5]. Methods for the analysis of biomaterials for Au are summarized in Table 28.3.

Industrial materials

The methods for the determination of Au in industrial materials (concentrates, sweeps and jewellery) are summarized in Table 28.4.

TABLE 28.4

Methods for the determination of gold in industrial materials

Material (amount)	Sample decomposition	Separation	Detection technique	DL ($\mu\text{g/g}$)	Ref.
Concentrates, mattes (2.5 g)	roasting, <i>aqua regia</i> (leaching), fusion with Na_2O_2	sorption on dehydrodithizone column, elution with thiourea	DCP-AES	n.g.	36, 37
Concentrates	HF - <i>aqua regia</i>		GF AAS	100	83
Bauxite residue	HF - HCl - HNO_3 (microwave assisted)	none	GF AAS	0.1 ^a	84
Slime	<i>aqua regia</i> (leaching)	extrn. with Aliquat 336 into DIBK	FAAS	1	8
Blister copper, Speiss products (5 g)	H_2SO_4 - <i>aqua regia</i>	amalgamation with Hg	AAS	1	85
Steel	HCl - HF , HNO_3	anion exchange of AuCl_4^-	RNAA	10	48
Pt-powder, Pt-chloride	<i>aqua regia</i>	anion exchange	GF AAS	24 ^b	32
Cyanide process solutions		extrn. as $\text{Au}(\text{CN})_2^-$ on a liquid membrane	FI FAAS	5 ^a	86
Wastewater (2 ml)		sorption on a TOPO modified tungsten wire	GF AAS	0.2 ^a	87

^a In the solution fed, ng/ml; ^b ADL, pg.

28.3.3 Accuracy considerations

Standard solutions

The stability of Au solutions is affected by exposure to bright sunlight and by base exchange reactions and adsorption on glass containers. Gold standard solutions (1 or 10 mg ml⁻¹) are available from reputable chemical suppliers. These solutions when stored in clean containers at

2–4°C in darkness should be stable for up to a year. Working solutions of 1 $\mu\text{g ml}^{-1}$ or less are stable for short periods and should be prepared daily.

Contamination

The contamination hazard is mainly associated with the earlier handling of samples containing high Au levels, such as sweeps and alloys. Contamination of the trace level fire assays by residues from high level gold assays is common unless separate pots, moulds, grinders are used for each of these operations. Measures to eliminate contamination problems have been discussed [88]. Special precautions to avoid contamination are necessary in the analysis of water and biological materials owing to the very low Au concentrations present.

Losses

The handling of traces of gold is hampered by different oxidation states, the tendency towards formation of coordination compounds and by kinetic indifference of many compounds. In all wet procedures the speciation of gold must be carefully considered as only active species can undergo the expected reactions. Care should always be taken to avoid the reduction of gold compounds to the metal which might occur, e.g. by overheating during evaporation or exposure to sunlight in glass containers. NaCl is added to form chlorocomplexes of Au to prevent the loss during the evaporation step [12]. The use of flexible tubing in peristaltic pumps was reported to adsorb Au in an uncontrolled manner [51].

Certified reference materials

A variety of CRMs are available for geological samples from the US Geological Survey and the Canada Centre for Mineral and Energy Technology (CANMET). For biological materials there are very few reliable data for gold in SRMs. The gold content in NBS Orchard leaves is estimated at $1.64 \pm 0.10 \text{ ng g}^{-1}$ and that in the Bowen's kale at $2.20 \pm 0.25 \text{ ng g}^{-1}$. Seawater standards with certified gold values do not exist. The ng/kg levels of gold are still not reliably determinable with any currently available method.

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Hafnium

Hafnium (Hf, atomic weight 178.49, melting point 2470°C, $d = 13.3 \text{ g cm}^{-3}$) is a grey lustrous metal. It occurs in the earth's crust with an average abundance of 4 ppm accompanying Zr to the extent of 1.5–2%. A few ores, e.g. alvite or thortveitite, show elevated Hf *vs* Zr ratios. Zirconium as a reactor material must not contain hafnium. As the chemical behaviours of Zr and Hf are virtually identical, analytical-chemical properties and the methods for separation and preconcentration of Hf are discussed together with those for Zr (*cf.* Chapter 66). Methods for the separation of Zr and Hf are based on the small differences in the stability of their fluoride, citrate, oxalate, formate and crown ether complexes and are discussed in Chapter 66 [1,2].

29.1 DETERMINATION

The very few approaches reported to the analysis of natural waters were based on TI MS [1]. The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratio is important in geochronometry since ^{176}Hf is the product of β -decay of ^{176}Lu [3]. Hafnium is determined in geomaterials after decomposition and further sample handling similar to that for Zr (*cf.* Chapter 66). Use of X-ray fluorescence, NAA, MS or AES is mandatory to reach the necessary degree of selectivity with respect to Zr. Spectrophotometry of Hf is essentially the same as that of Zr and is discussed in Chapter 66. X-ray fluorescence offers a DL of a few ppm even in the presence of the Zr matrix [4,5]. Instrumental NAA is the most widely used technique for Hf determination [6]. Data from INAA, RNAA, ID TI MS, SS MS and ICP MS for Zr and Hf in soil and meteorites have been compared [7]. Methods for the determination of Hf in real samples are summarized in Table 29.1.

TABLE 29.1

Methods for the determination of Hf in various samples

Material (amount)	Decomposition	Separation and/or preconcentration	Determin. technique	DL ($\mu\text{g/g}$)	Ref.
River, sea water (1 l)	none	copptn. with $\text{Fe}(\text{OH})_3$, dissoln. in HCl ; cation exchange	ID MS	n.g.	1
Geomaterials (0.5 g)	fusion with LiBO_2	cation exchange	ICP AES	n.g.	8
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. with HCl-HF	pptn. with cupferron	ICP MS	0.02	9
GeoCRMs	$\text{Na}_2\text{O}_2\text{-NaOH}$ fusion, dissoln. HCl	copptn. as $\text{Hf}(\text{OH})_4$, multistep ion exchange	RNAA	n.g	10
Mn nodules	HCl-HF	cation exchange	ID MS	n.g.	3
Scandium oxide (0.1–0.3 g)	$\text{HCl}, \text{H}_2\text{O}_2$	extrn. chromatography with 1-phenyl-3-methyl- 4-benzoyl-pyrazol-5-one	ICP AES	0.2	11
Yb matrix	n.g	extrn. chromatography of ^{177}W with TBT	RNAA	0.03	12
Zirconium dioxide	HCl-HF- H_2SO_4	anion exchange	ICP AES	n.g	13

Neutron activation analysis

Neutron activation analysis is based on the reaction $^{174}\text{Hf}(\text{n},\gamma)^{175}\text{Hf}$ ($t_{1/2} = 70$ d, $E_\gamma = 0.343$ MeV) or $^{180}\text{Hf}(\text{n},\gamma)^{181}\text{Hf}$ ($t_{1/2} = 42$ d, $E_\gamma = 0.133, 0.346, 0.482$ MeV). The ^{181}Hf nuclide can be determined by INAA by counting at the 0.133 MeV line with a DL of *ca* 80 ng [6]. Radiochemical separation is recommended for lower levels to avoid a high Compton background at this energy and the interferences by ^{152}Eu and $^{194\text{m}}\text{Ir}$ (at the 0.346 MeV and the 0.482 MeV lines, respectively) [7,14]. An alternative method is based on the reaction $^{176}\text{Hf}(\alpha,3\text{n})^{177}\text{W}$ and counting the ^{177}W nuclide after radiochemical purification [12].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of $10 \mu\text{g g}^{-1}$ at the most sensitive 277.34 and 263.97 nm lines. The relative intensities of almost two hundred Hf lines have been listed together with the measured critical concentration ratios for 115 lines for 34 possibly interfering elements [15]. Spectral interferences at the nine most sensitive Hf lines were shown to prevent the determination of Hf in rock, necessitating a separation step [9]. The 356.166 nm line was proposed for the determination of Hf in zirconium [16]. Aluminium [9] and Zr [16] were found to suppress the Hf signal.

Mass spectrometry

Correcting for mass fractionation in TI MS is difficult because the denominator isotope (^{180}Hf) is the heaviest one. The concentration measurements obtained from two different ratios ($^{177}\text{Hf}/^{180}\text{Hf}$ and $^{178}\text{Hf}/^{180}\text{Hf}$) should be taken into account [1]. In ICP MS the nuclide ^{178}Hf is typically monitored [9]. A method for the determination of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio by SIMS has been developed [17].

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Indium

Indium (In, atomic weight 114.8, melting point 157°C , $d = 7.3 \text{ g cm}^{-3}$) is a silvery-white, soft metal. It occurs in the earth's crust at an average abundance of 0.1 ppm and is obtained as a by-product of Zn smelting. Indium dissolves in dilute mineral acids with evolution of H_2 and in hot H_2SO_4 with the evolution of SO_2 . Indium exists in the III oxidation state. Indium salts are water soluble with the exception of carbonate, sulphide and phosphate. Alkalis precipitate $\text{In}(\text{OH})_3$ which is practically insoluble in excess of the reagent. Zinc, Cd, Mg and Al reduce $\text{In}(\text{III})$ to the metal. Indium forms halide, EDTA, oxalate and tartrate complexes. Indium is widely used in the electronics industry and metallurgy (as a hardener for some alloys) and has some uses in medicine (e.g. ^{111}In -labelled compounds).

30.1 SEPARATION AND PRECONCENTRATION

Extraction

Indium is readily extracted as InI_4^- , InBr_4^- or InCl_4^- from acidic media containing appropriate halides into oxygen-containing solvents (e.g. MIBK) [1–3]. Coextraction of iron is prevented by reducing $\text{Fe}(\text{III})$ with ascorbic acid [2,3]. Selectivity can be further improved by extraction of ion pairs of an In halide complex with higher amines (e.g. *n*-octylamine [4]), quaternary ammonium salts (e.g. Aliquat 336 or 336S [5,6,16]) or TOPO [7] into weakly polar solvents under carefully optimized conditions. Indium can be extracted at pH 4–9 with dithizone or DDTC [8]. The interferences are alleviated by masking and pH optimization. Indium can be extracted with di-(2-ethylhexyl)phosphoric acid [9,10] and with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one into MIBK [11].

Other methods

Indium can be separated by cation exchange from Fe, Ti, Si, Mn, alkali and alkaline earth metals [12], Cd–Hg–Te matrix [13] and thallium [14]. Anion exchangers [15] and chelating resins [16,17] have been less popular. Indium can be coprecipitated as hydroxide [18] or sulphide [19] with different carriers. *In situ* preconcentration of volatile indium hydride into a preheated graphite furnace coated with palladium has been reported [20].

30.2 DETERMINATION TECHNIQUES

Spectrophotometry

The most popular methods are based on the reaction of In with PAN ($\epsilon \approx 4.3 \times 10^4$ at 510 nm) or Eriochrome Cyanine R in the presence of CTA ($\epsilon \approx 1 \times 10^5$ at 585 nm). The selectivity is poor and a preliminary separation of In is required.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.8 \mu\text{g ml}^{-1}$ in the recommended air–C₂H₂ flame, oxidizing (lean, blue) at the most sensitive 303.9 and 325.76 nm lines. The detection limit can be improved by extraction of In as a halide complex into MIBK [3,11]. Continuous flow extraction of In with bis(2-ethylhexyl)phosphoric acid into MIBK coupled *on line* to FAAS was reported to give a DL of $0.02 \mu\text{g ml}^{-1}$ [10].

Graphite furnace atomic absorption spectrometry

Atomization of In from a pyrocoated tube or platform gives a characteristic mass of *ca* 10 pg at the 303.9 nm line. The determination of In is hampered by the high volatility of the element itself [21], the oxide [1] and especially the chloride [12,15]. Equilibria of In₂O in the GF have been discussed; losses below 1000 K are common [22]. Chloride should be totally removed from the solutions finally analyzed and a reducing atmosphere in the tube should be ensured [13]. A matrix modifier must be used. Magnesium nitrate alone was found to be unsuccessful [15]. In the presence of Pd the pyrolysis temperature can be increased to 1200°C in the aqueous solution [1,6,21,22]. Other matrix modifiers included Ni alone [12] or along with (NH₄)₂SO₄ or ascorbic acid [24], or a mixture of (NH₄)₂WO₄–tartaric acid [13]. Platform atomization was reported to reduce the interference of the HCl on the In signal [25]. Interferences from GaAs [25] and Fe [24] matrices have been studied.

Neutron activation analysis

Indium yields $^{114\text{m}}\text{In}$ ($t_{1/2} = 49$ d, $E_{\gamma} = 0.19$ MeV) and short-lived $^{116\text{m}}\text{In}$ ($t_{1/2} = 54$ min, $E_{\gamma} = 0.41$ MeV and others) after irradiation with neutrons [19]. Because of the very high cross-section radionuclide neutron sources are often sufficient. Radiochemical separation is necessary for trace analysis [9,20].

Other techniques

The fairly poor DL of ICP AES (ca 50 ng ml⁻¹ at the most sensitive 230.61 nm line) makes this seldom used for the determination of In unless in a multielement array (cf. Part II). Indium has two stable isotopes, ^{115}In and ^{113}In , with abundances of 95.67% and 4.33%, respectively. The former is overlapped by ^{114}CdH and the latter by ^{113}Cd so MS techniques are seldom used.

30.3 ANALYSIS OF REAL SAMPLES

Indium is widely dispersed in geological materials at very low concentration. Indium in rocks is usually quantified by GF AAS unless in a multielement array (cf. Section 9.3). Ores [1,24] and gallium arsenide are analyzed by GF AAS directly after sample decomposition [25–27]. The average concentration of In in plant and animal tissue is 10 ng g⁻¹ which can be determined on extraction preconcentration by GF AAS [6]. Methods for the determination of indium are summarized in Table 30.1.

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TABLE 30.1

Methods for the determination of In

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
River, seawater (50–400 ml)	none	copptn. with $\text{Hf}(\text{OH})_4$, dissoln. in HNO_3	GF AAS	0.2	18
River, seawater	none	<i>on-line</i> sorption on immobilized 8- hydroxyquinoline, elution with HCl-HNO_3	FAAS	3	17
Waste liquids	none	sorption on phosphor- amide chelating fibres, elution with HCl	ICP AES	n.g.	16
Rocks, sediments, soils (2 g)	HF , <i>aqua regia</i> , HBr-Br_2	extrn. as InBr_4^- (MIBK)	FAAS	200	3
Rocks (50–100 mg)	fusion with KOH	cation exchange, copptn. with 8- hydroxyquinoline	RNAA	1–3	19
Rocks (0.25 g)	fusion with Li_2CO_3 – H_3BO_3	cation exchange, anion exchange	GF AAS	n.g.	11
CRMs rocks, soils, sediments (0.25 g)	fusion with LiBO_2 , dissoln. in HBr	extrn. as InBr_4^- (MIBK)	GF AAS	50	2
CRM fly ash (0.3–1.2 g)	$\text{HF-H}_2\text{SO}_4$, fusion with KHSO_4	extrn. with dithizone (CCl_4), back-extrn. (HNO_3), extrn. with DDTC (CCl_4)	RNAA	500 ^a	8
CRM river sediments, fly ash (0.1–0.2 g)	HNO_3 – HClO_4 – HF	extrn. as InI_4^- (MIBK)	GF AAS	85	1
Rat tissues (0.5 g), blood, urine (0.5 ml)	H_2SO_4 , H_2O_2	extrn. with Aliquat 336 (hexane-MIBK), back- extrn. (HNO_3 – CH_3COOH)	GF AAS	5–10	6
CRM plant (0.3–1.2 g)	HNO_3 – H_2SO_4 – H_2O_2	extrn. with dithizone (CCl_4), back-extrn. (HNO_3), extrn. with DDTC (CCl_4)	RNAA	500	8

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Cadmium mercury telluride	HNO ₃	cation exchange, elution with HCl	GF AAS	n.g.	13
Zinc	HNO ₃	extrn. with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (MIBK)	FAAS	0.07 ^b	11
Aluminium (0.2 g)	HCl	extrn. as DDTC (xylene), back-extrn. (HNO ₃)	GF AAS	0.36	28
Lead, zinc	HNO ₃	ion exchange, elution with HNO ₃	GF AAS	0.60	15

^a Absolute detection limit, pg; ^b in the solution fed, ng/ml.

1535.

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Iridium

Iridium (Ir, atomic weight 192.22, melting point 2430°C, $d = 22.6 \text{ g cm}^{-3}$) is a silvery-white, hard noble metal, one of the Pt-group elements. Iridium occurs in the earth's crust with an average abundance of 1 ppb, usually as osmiridium in Pt ores. In bulk, it is not attacked by acids (incl. *aqua regia*) whereas the sponge is corroded very slowly. Iridium powder is dissolved in HCl in the presence of an oxidant, e.g. KClO_3 , when heated at 300°C in a Carius tube. The metal is readily attacked by fused alkali containing an oxidizing agent. Iridium occurs in all oxidation states from I to VI; Ir(IV) being the most stable. Alkalis precipitate the hydrous sesquioxide that is readily oxidized to dioxide to form a dark blue oxide, $\text{IrO}_2 \cdot 2 \text{H}_2\text{O}$. Iridium(IV) is reduced to Ir(III) with Fe(II) or ascorbic acid in an HCl medium. Stronger reductants, e.g. Zn reduce Ir(IV) to the metal. Permanganate or Ce(IV) oxidize Ir(III) to Ir(IV). Iridium(III) forms complexes with ammonia, cyanide and SnCl_3^- . Trace analysis for Ir is demanded primarily in geology. The analytical chemistry of Ir has been discussed in a number of monographs and review papers [1–4].

31.1 SEPARATION AND PRECONCENTRATION

Ion exchange

Ion exchange is based on the very stable IrCl_6^{2-} complex which is efficiently retained by anion exchangers [3,5–10]. Concentrated HNO_3 is sometimes used for elution [6,10] but more often the resin is ashed or decomposed by acid attack. Liquid chromatographic separation of Ir chloro [7,11], PAN [12] and oxine [13] complexes was discussed. Chelating resins have also been used [14–16].

Extraction

The IrCl_6^{2-} complex is readily extractable into oxygen-containing organic solvents while Ir(III) is retained in the aqueous phase. The presence of mild reducing agents thus permits a separation of Ir from Pt and Pd. Iridium can be separated from Rh in acidic medium by extraction of the ion pair of IrCl_6^{2-} with TPA, TBA or methyl-TPP. Chelating agents for the extractive separation of Ir are scarce.

Coprecipitation

In contrast to Pt and Pd, iridium does not precipitate when an acid solution is boiled with Te powder. Using Zn or Mg as reductors and Te as a carrier, however, Ir may be quantitatively precipitated especially when in the presence of a large amount of Pd [17,18]. The anionic Ir(III) complex with SnCl_3^- can associate with basic dyes to form sparingly soluble ion associates, and further, adducts, that can be separated by flotation [19,20]. Iridium (IV) can be separated from Rh(III) and Ru(III) by ion flotation in the presence of cationic surfactants [21].

31.2 DETERMINATION TECHNIQUES

Spectrophotometry

The yellow $\text{Ir}(\text{SnBr}_3)_6^{3-}$ complex is the basis of the spectrophotometric determination of Ir after its separation from Rh, Pt and Pd, either in the aqueous phase or on extraction into an oxygen-containing solvent. Flotation-spectrophotometric determination based on ion-associates of the $\text{Ir}(\text{SnCl}_3)_6^{3-}$ complex with basic dyes is more sensitive ($\epsilon \approx 3 \times 10^5$) [20]. Some azo- (PAN, PAR, TAR and sulphochlorophenolazorhodanine) and S-containing reagents (thiosalicylamide, dithiobenzoic acid, *N*- α -pyridyl-*N'*-benzoylthiourea) have been proposed. Catalytic methods have been reviewed [22].

Atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* 6–10 $\mu\text{g ml}^{-1}$ in the recommended C_2H_2 reducing flame at the most sensitive 264.0 or 266.5 nm lines. The sensitivity in the N_2O flame is 5 times higher. Flame AAS of Ir is interfered with by a number of common elements so matrix matching is necessary. Graphite furnace AAS offers a characteristic mass of *ca* 0.2 ng. Because of serious interferences from a number of elements (K, Ca, Na and Fe) and the rather poor sensitivity the separation and

enrichment of Ir prior to analysis are mandatory. Particularly convenient is coprecipitation with Te, which does not interfere because of the high pyrolysis temperatures (1400–1800°C) used [18]. Extraction is an alternative [23]. Platinum has been reported to be a favourable matrix for the determination of Ir [24].

Neutron activation analysis

Radioactive isotopes ^{192}Ir ($t_{1/2} = 74.5$ d) and ^{194}Ir ($t_{1/2} = 19$ h) with similar energies (about 0.30 MeV) are formed by irradiation of Ir with thermal neutrons. Many radionuclides, such as ^{51}Cr possess similar γ -energies, so a chemical separation has to be done prior to measurement [16,17,25,26].

Other techniques

ICP AES offers a DL of at the most sensitive 322.1 nm line. Iridium has two stable isotopes (^{191}Ir and ^{193}Ir with natural abundances of 37.3 and 62.7%, respectively) and is amenable to ID. ICP MS offers an ADL of 6 pg [10]. The ^{193}Ir was quantified whereas ^{191}Ir is used as a spike in isotope dilution [10]. Electrothermal vaporization sample introduction with Ni as matrix modifier has been proposed [27].

31.3 ANALYSIS OF REAL SAMPLES

Aqueous chemistry of Ir requires considerable experience because of slow kinetics of many reactions. When solutions of Ir are evaporated to dryness overheating of the residue should be avoided as compounds insoluble in water and acids may be formed. Procedures for the determination of Ir are summarized in Table 31.1.

Geological materials

The collection of Ir by lead fire assay is seriously affected by the flux composition and assay conditions because of the low affinity of Ir for lead. Addition of Au was proposed to improve the recoveries but severe losses were nevertheless experienced with basic or silicate slags and a re-assay was often necessary [28]. Losses on cupellation in a silver bead may be high but Au, Pt or Pt–Rh beads collect Ir quantitatively. Fire assay with NiS offers a quantitative recovery of Ir [27,29]. Fusion with Na_2O_2 [6,8,18] alone or with additions of alkali metal hydroxides [30] and borates [14] converts Ir into oxygen-containing anions of higher

TABLE 31.1

Procedures for the determination of iridium

Material (amount)	Sample decomposition	Separation	Detection technique	DL (ng/g)	Ref.
Rocks (0.5 g)	lead fire assay, fusion with NaOH–Na ₂ O ₂	none	NAA	0.01 –0.3	30
Rocks (10 g)	lead fire assay	cupellation in a gold bead	GF AAS	1	28
Rock, ore (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	NAA	0.5	17
Rocks	NiS fire assay, the bead dissolved in HCl	none	ID ETV ICP MS	n.g.	27
Sand, rock, ore (25 g)	NiS fire assay	none	INAA	0.2	26
CRMs (20–30 g)	NiS fire assay, the bead dissolved in HCl	none	ICP MS	0.1	29
Rock (5 g)	aqua regia–HF (bomb)	anion exchange	ETA AAS	17	5
CRMs coal and rock	fusion with NaOH–Na ₂ O ₂	anion exchange	NAA	1–9 ^b	8
Rock (5 g) ores (2 g)	HF– <i>aqua regia</i> (leaching), the residue fused with Na ₂ O ₂	copptn. with Te	GF AAS	40 ^c	18
Rocks	HF–HCl–HNO ₃ , fusion with Na ₂ O ₂ –NaOH	sorption on thiourea type resin	RNAA	0.1	29
Rocks	fusion with Na ₂ O ₂ –NaOH	extrn. with a long chain primary amine	RNAA	0.001	31
Rocks (0.5 g)	HNO ₃ –HF (bomb)	SPE on poly(vinyl- thiopropionamide) chelating resin	GF AAS	n.g.	15

Material (amount)	Sample decomposition	Separation	Detection technique	DL (ng/g)	Ref.
Rocks (0.5 g)	fusion with LiBO_2	sorption on polyDDTC resin	ICP AES	10–20	14
Rocks (0.2 g)	fusion with Na_2O_2 –NaOH	extrn. with N, N'-di- benzylidithiooxamide in the presence of I^- (CHCl_3)	NAA	0.002	32
Sediments, Mn nodules, CRMs (0.5–1 g)	fusion with Na_2O_2	anion exchange, elution with hot HNO_3 , sorption on a single anion exchange bead, stripped with HCl	GF AAS	20 ^b	6
Sediments (0.5–1 g)	HF – HNO_3 (microwave assisted)	anion exchange, elution with 12 M HNO_3	ID ICP MS	6 ^b	10
Sweeps	fusion with Na_2CO_3 – Na_2O_2	pptn. with formic acid	AAS ICP AES DCP AES	0.5–5 ^a	33
Sweeps	NiS fire assay	filtration of the sulfide, dissoln. in <i>aqua regia</i>	AAS ICP-AAS DCP AES	0.5–5 ^a	33
Concentrate	dissoln. in HCl	anion exchange, LC	UV	0.1 ^a	7
Steel	dissoln. in HCl–HF, HNO_3	anion-exchange of IrCl_6^{3-}	RNAA	10 ^b	9
High-purity Pt (0.05–0.1 g)	pressure dissoln. in <i>aqua regia</i>	sepn. of the Pt matrix by extrn. with i-PeOH– MIBK	GF AAS	2000	24

^a In ppb in solution; ^b absolute detection limit, pg; ^c sensitivity, pg.

valence states that are readily soluble in mineral acids. Iridium is precipitated by reduction with an alkali formate after degradation of the peroxide by boiling.

Industrial materials

Concentrates, slags, mattes, sweeps and alloys require a method applicable to Ir concentrations ranging from $\mu\text{g g}^{-1}$ to percent levels in the presence of large concentrations of other elements. The recommended methods are based either on fusion with Na_2O_2 followed by the dissolution of the melt in acid or on the NiS fire assay collection followed by the dissolution of the bead in *aqua regia* [2].

Other samples

Little is known about the presence of Ir in sea and fresh waters. The only method hitherto published enabled the determination $0.9 \mu\text{g l}^{-1}$ of Ir in seawater based on a 100-l sample. Iridium was preconcentrated as the anionic chloride complex on ion exchange resins [6]. Upon elution from the column it was further purified and concentrated by adsorption onto a single ion exchange bead, stripped with hot concentrated HNO_3 and determined by GF AAS. The recovery varied from sample to sample and the accuracy is unknown.

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Iron

Iron (Fe, atomic weight 55.85, melting point 1535°C , $d = 7.9 \text{ g cm}^{-3}$) is a shiny, malleable metal with ferromagnetic properties. It is very abundant in the earth's crust (*ca* 4.7%), occurring primarily in oxidic ores: haematite and magnetite. Iron is the main component of steels and is considered to be a biologically essential element. Iron is a reactive metal, soluble in HCl and H_2SO_4 . It occurs in two oxidation states II and III, the latter being more stable. In aqueous solution iron may occur as the ferrous Fe^{2+} and the ferric Fe^{3+} ion. The latter is susceptible to hydrolysis to form insoluble ferric hydroxide polymers generally referred to as rust. The hydroxides, $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, precipitate at above pH ~ 7.5 and 2–3, respectively; neither of them shows acidic properties. Iron(III) forms stable fluoride, chloride, cyanide, EDTA, tartrate and oxalate complexes. Iron(II) forms a stable ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$ ion. In acid media Fe(III) acts as oxidant.

32.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Separation and preconcentration are generally avoided unless ultra-trace analysis is required. Iron(III) is usually precipitated as $\text{Fe}(\text{OH})_3$. When the precipitation is carried out with $\text{NH}_3(\text{aq})$, $\text{Al}(\text{OH})_3$ can be used as collector; otherwise $\text{La}(\text{OH})_3$ is recommended. Iron(III and II) was quantitatively separated on immobilized 8-hydroxyquinoline [1,2]. Trace amounts of iron are efficiently extracted as FeCl_4^- from 6–8 M HCl into oxygen-containing solvents (MIBK, ethers), together with Ga, Tl(III), Au(III), Ge, As, Sb and Mo. Iron(III) can also be extracted as the thiocyanate complex into oxygen-containing solvents which used to be combined with the spectrophotometric determination of Fe.

Spectrophotometry

The widest popularity is enjoyed by the 1,10-phenanthroline and bathophenanthroline methods because of their high selectivity, reasonably high sensitivity ($\epsilon = 1.1 \times 10^4$ at 512 nm and $\epsilon = 2.2 \times 10^4$ at 553 nm) and the adaptability to the FI mode. Iron(II) and total iron [after reduction of Fe(III) to Fe(II)] can be determined. The reaction is carried out in acetate or citrate buffers. Iron (III) can be reduced by hydroxylamine in a weakly acidic medium (pH 3–4) or by ascorbic acid in a more acidic solution (pH 0–1). None of the hundreds of methods reported in the literature was able to match the phenanthroline method in terms of the overall performance and is not expected to do in near future.

Chemiluminescence

Chemiluminescence determinations of Fe(III) using the luminol- H_2O_2 system [1] or Fe(II) using Brilliant Sulphoflavin and H_2O_2 (pH 6–7) [2] offer excellent sensitivity, and are readily amenable to FI mode but lack in many cases the required selectivity, making the separation of iron, e.g. by ion exchange, necessary [2].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.1 \mu\text{g ml}^{-1}$ at the most sensitive 248.3 nm line in the recommended air- C_2H_2 , oxidizing (lean, blue) flame. With multielement lamps containing cobalt, an interference may occur when using the 248.3 nm iron line. A reduction in sensitivity is observed in the presence of Co, Cu and Ni. These interferences are strongly dependent on the flame conditions and can be controlled by using a very lean (hot) flame. The suppression of the iron signal by silicon can be overcome by the addition of CaCl_2 . Reduction of the iron signal caused by organic acids (citric acid in particular) can be eliminated by the addition of H_3PO_4 , or NaCl.

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 5 pg (DL of 0.02 ng ml^{-1}) using pyrocoated tube and platform atomization. Addition of H_2 to the Ar purge gas improved the peak shape, peak height and reproducibility, reduced the noise and resulted in the prolonged tube lifetime [3]. $\text{Mg}(\text{NO}_3)_2$ is the usual matrix modifier; ascorbic acid [4] and Ni [5] were also proposed, the latter for the sulphate matrix. The iron signal is strongly affected by the HNO_3 concentration [6]. Boric acid decreased the intensity of the iron peak, made the signal broader and caused a higher background [7].

Atomic emission spectrometry

Atomic emission spectrometry with the ICP excitation offers DLs of 2–5 ng ml⁻¹ at the most sensitive 238.20, 259.94, 239.56 and 234.35 nm lines. Cobalt overlaps at 238.20 and 239.56 nm and Ni at 234.35 nm. The choice of Fe lines in the Zr matrix has been discussed [8]. Direct sample insertion and external ETV of powders have been studied; the addition of thermochemical substances [(C₂F₄)_n, NaF] is often necessary to achieve complete evaporation of Fe [9]. The graphite cup insertion technique was applied to the direct determination of Fe in lead and zinc metals on selective evaporation of the matrix [10]. Direct current plasma AES has been discussed [11].

Mass spectrometry

Iron has four stable isotopes: ⁵⁴Fe (5.81%), ⁵⁶Fe (91.75%), ⁵⁷Fe (2.15%) and ⁵⁸Fe (0.29%). In ICP MS detection limits of 4 pg ml⁻¹ for ⁵⁶Fe, 50 pg ml⁻¹ for both ⁵⁴Fe and ⁵⁷Fe and 1300 pg ml⁻¹ for ⁵⁸Fe have been reported [12]. All the isotopes are overlapped with polyatomic ions [13]: for ⁵⁴Fe: ⁴⁰Ar¹⁴N, ⁴⁰Ca¹⁴N, ³⁷Cl¹⁷O, ³⁷Cl¹⁶OH; for ⁵⁶Fe: ⁴⁰Ar¹⁶O, ⁴⁰Ca¹⁶O; for ⁵⁷Fe: ⁴⁰Ar¹⁷O, ⁴⁰Ca¹⁷O. The interference from ⁵⁴Cr could be corrected instrumentally whereas ⁵⁸Ni had to be removed beforehand [12,14]. In ID ICP MS use of ⁵⁴Fe as the reference isotope and ⁵⁷Fe as the spike has been recommended [12]. Other workers sometimes found the interference at mass 54 from ⁴⁰Ar¹⁴N⁺ to be too high to allow meaningful results and preferred the ⁵⁷Fe [13,15]. Cryogenic desolvation was used to reduce (36-fold) ArO⁺ interference; ArN⁺ was, however, enhanced by a factor of 2 [16]. Sample introduction by ETV significantly reduces the levels of ⁴⁰Ar¹⁴N and ⁴⁰Ar¹⁶O [17,18] and offers an ADL of 0.3 pg. ICP MS is the most widely used technique for the determination of iron stable biotracers [12,17,19]. Fast atom bombardment MS was used to determine the ⁵⁸Fe/⁵⁶Fe ratios in clinical materials; solvent extraction [14] and anion exchange [20] have been used to remove the interfering ions. Introduction of gaseous Fe(PF₃) for the stable isotope analysis of iron by EI MS has been presented [21]. An improved MS technique utilizing ion pulse counting detection and an absolute iron isotope abundance standard for calibration has been described for iron isotopic analysis [22].

Neutron activation analysis

Neutron activation analysis of iron is based on the reaction ⁵⁸Fe(n,γ)⁵⁹Fe and counting the ⁵⁹Fe (*t*_{1/2} = 45.1 d, *E*_γ = 1.10 and 1.29

MeV) nuclide. The sensitivity is low because of the low isotopic abundance and small reaction cross-section of ^{58}Fe . ^{59}Fe is masked by ^{60}Co activity so a radiochemical separation of iron is required [23].

32.2 ANALYSIS OF REAL SAMPLES

The large abundance of Fe in geochemical samples makes its trace determination irrelevant. Determination of the total iron in environmental and biological materials is generally not a problem; the present efforts are focused on the automation of the systems and speciation of iron. Biochemistry and environmental chemistry of iron has been reviewed [24].

Water

Concentrations of Fe in the surface water are at the sub-mg l⁻¹ level and can be determined directly. Effect of acidification and filtration of samples on iron content measured in surface waters was studied [11]. The accurate determination of Fe in open seawater and ocean water is hindered by its low concentration (down to 0.1 ng l⁻¹ [24]) and ubiquitous risk of contamination. The most common methods based on the extraction of dissolved iron from large volumes of filtered seawater followed by GF AAS detection require a great deal of sample manipulation, all of which must be done in ultraclean conditions by personnel trained in clean laboratory techniques. An ion exchange separation–preconcentration followed by chemiluminescent detection was found to be the most promising [2]. Severe iron contamination of Amberlite XAD-4, Amberlite XAD-7, C₁₈ silica and Muromac A-1 has been reported [1]. The influence of freezing of aqueous samples on the Fe(II)/Fe(III) equilibrium has been investigated; no change was observed in the pH range 2–5, irrespective of the freezing temperature [25].

Biological samples

Serum, body fluids and urine are analyzed directly usually by GF AAS [26–29] or upon dilution by ICP AES [30]. Blood was digested with HNO₃–HCl *on line* using microwaves [31]. Determination of iron stable tracers (and isotope ratios) administered for medical purposes in human faecal matter [12,14], serum [17] and blood [19] by using MS techniques is gaining popularity. The fairly high concentrations of Fe in foods make FI slurry sampling FAAS (DL 0.2 µg ml⁻¹) popular [32]. Digestion of animal tissue with HNO₃–H₂SO₄, conventional [33,34] or microwave-assisted [33,35,36] is an alternative. Iron in oils and fats can

be determined directly by FI FAAS [37] or GF AAS [38–40]; results of collaborative studies have been reported [38,39]. Ultrasonically assisted extraction of iron from edible oil samples into 1 M HNO₃ has been proposed [41]. Beverages, e.g. beer, can be analyzed by FIA FAAS directly after decarbonation [42].

Industrial materials

Trace Fe impurities in industrial materials are commonly determined in a multielement array as discussed in Chapters 11 and 12. Determination of Fe in pure gold [43] and in Zr salts [8,44] has been reported. A modified atomic absorption spectrometer for the determination of Fe in gaseous hydrogen chloride has been developed [45].

32.3 SPECIATION

Redox speciation of iron is important for understanding the role of this metal in biogeochemical cycles. Chemical species of Fe in aqueous and particulate fractions of atmospheric aerosols have been studied using ion-chromatography with photometric, AAS and TXRF detection [46]. An operational scheme for speciation of iron in river water has been proposed [47]. Simultaneous determination of Fe(III) and Fe(II) using a single detector and a single injection has been described [48]. Most methods are based on the determination of one of the iron species by spectrophotometry or chemiluminescence followed by the determination of the total Fe after reduction or oxidation. Fe(II) and Fe(III) can be separated using cation exchangers or ion pair chromatography.

Iron in plasma is bound by porphyrins (haem iron) or by proteins (ferritin, transferrin, albumin and others) which are separated by size-exclusion or ion exchange chromatography. Selective protein precipitation with CCl₃COOH followed by ICP MS results in assay only of transferrin and total free iron [49]. Speciation schemes for wine [62] and beverages [50] have been proposed; many low weight soluble Fe complexes (ascorbic acid, citrate, amines, amino acids) were present. Speciation of natural iron porphyrins is gaining increased interest [51–53]. Methods for speciation of iron are summarized in Table 32.1.

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TABLE 32.1

Analytical methods for the simultaneous speciation of iron

Sample (amount)	Species determined	Chromatography (eluent)	Detection technique	Ref.
Standards	ferritin, hemo-globin, myoglobin, cytochrome-c	size-exclusion [0.2 M $(\text{NH}_4)_2\text{SO}_4$, 0.05 M Tris-HCl, pH 7.0]	ICP MS	54
Standards	Fe(II), Fe (III)	<i>on-line</i> sorption of the Fe(II)–ferrozine complex on a C_{18} column, elution with MeOH	FI AAS	55
Humus soils leachates	macromolecular complexes	size-exclusion (0.2 M $\text{CH}_3\text{COONH}_4$, pH 3.6–5.2)	ICP MS	56
Natural waters	macromolecular biocomplexes	size-exclusion (16 mM K_2HPO_4 , pH 7.3)	GF AAS ICP AES	57
Serum, milk, seminal fluid	proteins	size-exclusion (0.1 M HEPES, 0.1 M NaCl, pH 7.4)	ICP AES	58
Serum	Fe-proteins	anion exchange [gradient elution from 0.05 M Tris-HCl (pH 9.2) to 0.05 M Tris-NaCl (pH 9.2)]	GF AAS	59
Plasma	apolactoferrin, mono- and diferric lactoferrins	cation exchange (I: 50 mM NaCl, II: 90 mM NaCl, III: 200 mM NaCl in 0.02 M acetate, buffer, pH 5.4)	UV	60
Human milk	apolactoferrin, mono- and diferric lactoferrins	cation exchange (gradient elution with 10 mM sodium Phosphate buffer, pH 7.0)	UV	61
Wine (8–50 ml)	Fe(II), Fe(III)	cation exchange (2.25 M HCl)	FAAS	62
Wine (1–10 ml)	uncharged organic Fe	sorption at pH 2.8 on Amberlite XAD-2	FAAS	62
Wine (3–20 ml)	ionic Fe(III)	anion exchange as citrate complex (2 M HCl)	FAAS	62
Pharmaceutical products	ferritin	size-exclusion (0.07 M KH_2PO_4 , 1 M NaClO_4 , 0.1 mM NaN_2 , pH 6.8)	ICP AES	63
Coals oil shale	porphyrins	high temperature GC	ICP MS	51
Crude oils	porphyrins	high temperature GC	MIP AES	52, 53

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Lead

Lead (Pb, atomic weight 207.19, melting point 328°C , $d = 11.35 \text{ g cm}^{-3}$) is a malleable, soft, silvery-grey metal. It occurs in the earth's crust with an average abundance of 16 ppm, primarily as galena (PbS). The metal dissolves readily in HNO_3 , CH_3COOH (in the presence of oxygen, slowly in HCl and remains unattacked by (unless anhydrous) H_2SO_4). The most common oxidation state is Pb(II) albeit Pb(IV) and Pb(–IV) (plumbane) are also well characterized. In aqueous media the Pb^{2+} ion, which hydrolyzes readily, is present. The hydroxide, $\text{Pb}(\text{OH})_2$, precipitates within the pH range 7–13 and is amphoteric. Lead(II) nitrate, acetate, chlorate and perchlorate are water soluble. Lead(II) forms tartrate, acetate, thiosulphate and EDTA complexes. Lead powder is a fairly strong reductant both in acidic and alkaline media. Lead(IV) is a strong oxidant. A wide range of organometallic compounds of the type PbA_{4-n}^{n+} , where $n = 0, 1, 2, 3$ and A denotes alkyl, are known.

The presence of Pb in the environment is ubiquitous and is due to its widespread industrial uses including that of tetraalkyllead compounds as antiknock additives to gasoline. All forms of Pb are poisonous and the need for trace analysis is primarily related to ecological and clinical toxicology and occupational health. The Pb isotope ratios are subject to change with geological time and can be used in geochronometry and for the identification pollution sources.

33.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of Pb as dithizonate from neutral or slightly alkaline solution in the presence of citrate and cyanide into non-polar solvents

followed by back-extraction into HNO_3 is very selective [1,2]. Lead is readily extracted with dithiocarbamates from slightly acidic or neutral (containing citrate) media, usually into MIBK or hexane [3,4] and can be stripped with HNO_3 or Hg(II) solution. Cadmium interferes unless complexed. In the presence of large amounts of Cd, extraction of Pb as dithizonate or as an ion pair of PbI_4^{2-} [5,6] or salicylate [7] with high molecular weight amines or quaternary ammonium salts has been recommended.

Volatilization

The slow kinetics and poor efficiency of the plumbane generation are improved by adding an oxidant before the injection of NaBH_4 [8–12]. The $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--HNO}_3$ system is the most efficient but suffers from high blanks and poor selectivity *vs* other hydride forming elements [13,14]. The use of H_2O_2 in a mixture with HClO_4 , HNO_3 or HCl gives the best compromise in terms of sensitivity, reagent blank and interference effects [15–29]. A lactic acid medium was found to be exceptionally suitable for the PbH_4 generation in the presence of $\text{K}_2\text{Cr}_2\text{O}_7$ [13]. Surfactants, e.g. CTA, were found to accelerate generation of PbH_4 in the $\text{K}_2\text{S}_2\text{O}_8\text{--HNO}_3$ medium [20]. High Cu and Fe contents should be masked with NaCN and sulphosalicylic acid, respectively [2], or removed [13]. The interference with complexing agents such as EDTA was alleviated by the addition of Zn^{2+} [15]. Some transition metals (especially Ni) enhance the PbH_4 generation efficiency [18,19]. Plumbane can also be generated in organic media [21,22] and slurries [12,23,24]. An alternative to the plumbane generation is the reaction of lead with NaBEt_4 to produce the volatile $\text{Pb}(\text{C}_2\text{H}_5)_4$ which can be trapped in a graphite furnace [25].

Sorption

Whereas simple ion exchange is seldom used [26–28] chelating resins, especially with immobilized 8-hydroxyquinoline [29,30] and poly(dithiocarbamate) [31], enjoy wider popularity. Iron, Cu, Al and Zn interfere and should be masked with triethanolamine, thiourea, fluoride, acetylacetone or cyanide [29]. Lead–DTC complexes can be sorbed on microcolumns with activated alumina [32] or C_{18} [33].

Precipitation

Precipitation of Pb as DTC complexes with Cu, Fe and Ni carriers is popular [34,35]. Lead trifluoroethylxanthate has been precipitated onto

microcrystalline naphthalene [36]. A continuous precipitation of Pb^{2+} with $\text{NH}_3(\text{aq})$ gave a concentration factor up to 700 [37]. Electrodeposition of Pb on graphite platforms has been widely used [38–40].

33.2 DETERMINATION TECHNIQUES

Spectrophotometry

The dithizone method ($\epsilon = 6.9 \times 10^4$ at 520 nm) is the most popular. Selectivity is achieved in an alkaline solution (pH 9–11.5) in the presence of citrate, cyanide and hydroxylamine. Bismuth and Tl are extracted together with Pb and, if present, should be removed by preliminary extraction at pH 2–2.5 [41].

Flame atomic absorption spectrometry

Flame AAS offers a DL of 0.02–0.1 $\mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 oxidizing (lean, blue) flame at the most sensitive 283.3 nm line. Spectral enhancement in Ca rich matrices has been observed [42]. The 217.0 nm line can be interfered with by Cu. The interferences of Fe, Al, Ca and Ba are alleviated by adding ascorbic acid [43]. Interferences are more pronounced in HCl than in the HNO_3 medium [44]. Ion exchange [29,31,45], solvent extraction [4–6,38], and precipitation [37, 46] have been used to improve sensitivity and selectivity.

Quartz furnace atomic absorption spectrometry

Atom-trapping in a water-cooled silica tube placed in an air– C_2H_2 flame enhances the sensitivity compared with FAAS [12,47–49]. Quartz furnace AAS has been commonly used in combination with hydride generation [9,13,18] or volatilization of Pb as $\text{Pb}(\text{C}_2\text{H}_5)_4$ [50] and allowed DLs down to 0.1 ng ml^{-1} to be obtained. It is the most widely used detection technique in GC of organolead species (*cf.* Section 33.4.1.).

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of *ca* 0.05 ng ml^{-1} but is prone to interferences due to the complex atomization mechanism of Pb. Non-specific absorption and loss of lead by volatilization either as halides or as organic lead compounds are the main problems. Sodium, Mg and Ca chloride or sulphide are the most serious interferents [51]. A matrix modifier is essential to raise the charring temperature to 1200°C. Palladium, which forms a thermally stable alloy with Pb, is the most

popular [3,52–55]. The common alternative is $\text{NH}_4\text{H}_2\text{PO}_4$ [34,56–59] or its mixture with $\text{Mg}(\text{NO}_3)_2$ [56,60,61] but a high background from the volatilized $\text{NH}_4\text{H}_2\text{PO}_4$ is likely. The interference mechanism for sulphate has been discussed [62]. The interference is decreased by addition of La [63,64] or ascorbic acid [65]; the latter may lead to double peaks with use of the non-pyrolytic tube [66]. Spectral interferences due to S_2 molecules have been discussed [67]. A mixture of NH_4Cl and CrCl_3 was proposed to remove the background from the Ga matrix [68]. The use of a L'vov platform is beneficial [58,63,64]. The use of the Zeeman background correction is essential. Hydrogen was added to the purge gas [69,70] to alleviate the matrix suppression effect. Sensitivity of GF AAS can be improved by the electrodeposition of lead on pyrolytic graphite platforms [39,40,71] or trapping of PbEt_4 [25,50] or PbH_4 [72] in the furnace. A Zeeman scanning AAS technique was used for the determination of lead isotope distributions [73].

Slurry sampling can be valid provided that the concentration is 3–5% [23,74–78] and efficient matrix modification is applied. A Pd–Mg nitrate mixture has been systematically studied [79] and was found to be the best [79–82,84]. Others included $(\text{NH}_4)_3\text{PO}_4$ [85], $(\text{NH}_4)_2\text{HPO}_4$ [78], $\text{NH}_4\text{H}_2\text{PO}_4$ [77,86]. An oxygen ashing step helps remove the organic matter [77]. Soil [79,80,87] and alumina [88,89] slurries could be successfully analyzed up to a particle size of 20 μm . Solid sampling GF AAS has been discussed [78,90] and wall, platform and probe atomization have been compared [91].

Plasma source atomic emission spectrometry

The sensitivity of ICP AES ($10\text{--}30\text{ ng ml}^{-1}$) is fairly poor and the most intense emission lines (220.35, 283.32 and 405.78 nm) suffer from spectral interference from Al, Fe, Ca and Mg. A better performance was reported after hydride generation [16,17,20], ETV [92] and electrical vaporization from membrane filters [93]. Still lower DLs (down to a few pg) can be obtained by ETV MIP [94,95] or CMP [96,97]. The MIP is a particularly convenient detection technique for GC allowing sub-pg DLs to be obtained (*cf.* Section 33.4).

Atomic fluorescence spectrometry

Non-dispersive AFS with gaseous sample introduction into an Ar– H_2 flame offers DLs down to several pg [15,98]. Detection limits down to the level of a few femtogram can be obtained by ETV LE AFS which is readily applicable to the direct analysis of a variety of samples [99–103].

Mass spectrometry

Lead has four naturally occurring isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb with the relative abundances of 1.0, 25.1, 21.7 and 52.2%, respectively. Thermal ionization MS offers excellent accuracy and precision for the isotopic ratio determination [28] and for IDA [104,105]. Inductively coupled plasma MS offers a DL of 0.01–0.05 ng ml⁻¹ which is usually blank controlled. The technique can be used with internal standard calibration [61] but IDA offers better precision and accuracy [106–108]. A combination of isotope dilution and standard addition quantification was used to minimize matrix suppression in ethanolic media [109]. ICP MS enables rapid acquisition of isotopic ratio data at the expense of precision [2,36,110–116]. The latter can be increased by the use of internal standards such as ^{203}Tl and ^{205}Tl [117]. High precision determination of Pb isotope ratios by ICP multiple-collector MS has been reported [118]. The potential of ETV ICP MS [110] and LA ICP MS [119] as rapid survey techniques for lead isotope ratios has been emphasized. Interlaboratory comparison study on lead isotope ratios determined by ICP MS has been undertaken [120]. The use of ID GD MS has been reported [121]:

33.3 ANALYSIS OF REAL SAMPLES

Lead is ubiquitously present in all kinds of samples and is often determined in a multielement array (*cf.* Part II). The determination of Pb is usually based either on direct measurement or on sample dissolution because of the contamination risk. Below some specific considerations to various sample types are specified.

33.3.1 Environmental and geological materials

Air particulates, dust and sediments

Direct analysis by GF AAS [69,122–126], plasma emission [93] or XRF [124,127,128] are widely used for the determination of lead in dust [69,127], air aerosol [10,93,122,125,126,128] and water-borne particulates [123] and fly ashes [124]. Near-real-time impaction GF AAS was found to be promising [122,125] for air particulates. High temperature ashing is prone to significant losses so the filter should be destroyed by low-temperature combustion in an oxygen plasma or by a wet procedure. Lead is quantitatively extracted by hot HNO_3 or a mixture of

HF-HNO₃ [124]. Real-time determination of femtogram amounts of Pb in individual airborne particles by ICP MS with direct air sample introduction has been developed [11].

Water

Preservation of drinking water to be analyzed for Pb has been discussed [129]. Flame AAS is not sufficiently sensitive for the direct analysis of the natural and drinking waters and is usually applied upon *on-line* sorption [27,29,32,45,130]. Direct ICP MS is becoming the technique of choice. An *on-line* method for the determination of lead (DL 0.9 pg ml⁻¹ for 5-ml sample) and lead isotope ratios in fresh and saline waters has been developed [116]. Thermal ionization MS is particularly sensitive and accurate but requires a cumbersome sample preparation procedure [104,105]. Laser-excited AFS has been used for the direct analysis of freshwater [100], seawater [101] and precipitations from remote areas [97] with DLs down to the low pg ml⁻¹ level. Lead complexed with humic and fulvic acids was sorbed from fresh water samples was retained by anion exchange [131] or Amberlite XAD-2 [132] and determined by GF AAS.

Soils and sediments

These can be analyzed as slurries [14,75,78–82,87]. Lead in soil is mostly adsorbed on the particles rather than occluded in them and can be released by leaching of the sample with HNO₃ and *aqua regia* without complete destruction of the silicate structure (*cf.* Section 9.4). Total decomposition with HNO₃-HF-HClO₄ is essential for spike equilibration in ID ICP MS [107]. X-ray fluorescence, AAS and AES have been compared for the analysis of soils [133]. Different strategies to assess Pb mobilization in polluted river sediments have been evaluated [134]. Lead is often subject to speciation studies according to the scheme discussed in Section 9.6.

Rocks and ores

Galena should be dissolved in concentrated HCl rather than HNO₃ as the latter oxidizes sulphur to sulphate with the formation of sparingly soluble PbSO₄ [2,110]. Use of H₂SO₄ should also be avoided. Lead is often determined for dating in U ores which are decomposed by HNO₃, HF, HClO₄ [110,135], also with microwave assistance [135].

33.3.2 Biological materials

Clinical samples

Blood is usually analyzed directly [136], upon dilution with Triton X-100 [60,111,137,138], and a matrix modifier, usually $\text{Pd}(\text{NO}_3)_2$ – $\text{Mg}(\text{NO}_3)_2$ [60] but also $(\text{NH}_4)_2\text{HPO}_4$ [59,137–139] with DLs down to 0.5 ng ml^{-1} . The aspecific matrix background is alleviated by platform atomization and Zeeman correction. Flame AAS on protein precipitation has been developed [140]. Inductively coupled plasma MS is rapidly gaining popularity; it has been proposed for the determination of lead isotopic ratios after dilution with matrix modifier and Triton X-100 [111,112]. Electrothermal vaporization ID ICP MS is particularly sensitive and accurate [141]. Determination of Pb in blood has been the subject of several comparison studies [142–145]; the use of GF AAS has been reviewed [146]. Protocols have also been described for the preparation and characterization of quality control materials [140,147–151]. The determination of Pb in blood by TXRF has been discussed [152]. Urine samples were stabilized with 1–3% acetic acid to avoid the precipitation of $\text{Ca}_3(\text{PO}_4)_2$ which might entrain some of the lead [38]. Samples are analyzed by GF AAS on dilution with matrix modifier, usually $\text{Pd}(\text{NO}_3)_2$ – $\text{Mg}(\text{NO}_3)_2$ [56] but extraction with APDC into MIBK followed by GF AAS [3] or FI FAAS [38] was also reported. Seminal fluid was analyzed after deproteinization with HNO_3 , without a matrix modifier, with a DL of 1.4 ng ml^{-1} [153]. Teeth [111,154] and bone [42,57] were analyzed by GF AAS [42,57,154] or ICP MS [111] on dissolution with HNO_3 , also microwave assisted [42]. The analysis for Pb in teeth has been reviewed [155].

Food, plant and animal tissues

Food, plant and animal tissues can be analyzed as slurries directly [77,156] or upon partial wet oxidation [157] with a DL down to 0.5 ng g^{-1} . Destruction of organic matter prior to analysis is prone to losses. Dry ashing is seldom used [158]. Wet digestion is the usual choice. Nitric acid alone is unable to decompose tissues rich in lipids [1,106]; addition of V_2O_5 [13,18,159] or H_2O_2 [158] was recommended. The presence of H_2SO_4 should be avoided since it may result in losses due to the precipitation of PbSO_4 [158] and signal suppression in GF AAS [52,65]; the latter can be prevented by ascorbic acid as matrix modifier [65]. The HNO_3 – HClO_4 mixture was the most efficient [34,52,160]. Flame [6,13], GF AAS [1,4,19,34,57,61,159] and HG AAS [8,22] have

usually been used but ICP MS is gaining popularity [106–108]. Direct analysis of the digests is preferred but extraction is recommended in the presence of high levels of Cd (some shellfish) for FAAS [6]. Extraction with APDC–DDTC with subsequent stripping with Hg(II) allowed for the interference-free determination by GF AAS [4]. Wine and fruit juice have been analyzed directly on dilution [58,161] or on digestion with HNO₃ (pressure [84] or microwave [12] assisted) by a variety of techniques. Fruit juices have been analyzed by HG ICP AES with a DL of 9 ng l⁻¹ [20]. Results of collaborative study on the direct GF AAS determination of Pb in edible oils and fats have been presented [162].

33.3.3 Industrial materials

Gasoline

The total of lead is usually determined either on dilution with DMF or propan-2-ol [25,163] or after oxidation of tetraalkyllead with I₂ [164,165] or ICl [166]. Iodine combines with the lead to produce less flame-refractory compounds [163]. Water-soluble iodides can be extracted into dilute HNO₃ before the GF AAS determination [164]. Calibration with aqueous standards was found to be satisfactory [164]. An FI method for the total lead determination in gasoline has been developed [165]. Gasoline may be analyzed for particular alkyllead compounds on dilution by GC with an element selective detector (*cf.* Section 33.4.).

Alloys and chemicals

Copper-based alloys were dissolved in HCl–HNO₃ [48,49]. Silver wire was anodically dissolved in diluted HNO₃–H₂SO₄ with subsequent removal of the Ag matrix by a second electrolysis with a Pt anode prior to Pb determination by GF AAS [167]. D₂ background correction was sufficient for the determination of Pb in Ni-based alloys by GF AAS without a matrix modifier and with calibration with aqueous standards [168]. Lead was determined in high purity palladium aminodichloride and aminodinitrite [169] and gallium arsenide [68].

Other samples

Paints and pigments are mineralized in HNO₃ prior to FAAS [170] or ICP MS [111]. Pigment slurries have been analyzed by GF AAS [159]. Polymers are analyzed by FAAS [171,172] or GF AAS [173] on simple dissolution with DMF [172,173]. Dissolution with H₂SO₄–H₂O₂ [171]

results in the formation of insoluble lead and alkaline earth metal sulphates and must be followed by treatment with EDTA in NH_3aq [171]. Direct plasma emission determination of lead in lubricating oil has been reported [93]. Determination of Pb in oils and fats was subject to a collaborative study [174]. Isotope dilution GD MS was used for the analysis of waste oil samples after leaching Pb with water [121]. Alumina catalysts were digested with HF in a microwave [175].

33.4 SPECIATION OF ORGANOLEAD COMPOUNDS

Tetraalkyllead compounds ($\text{Me}_n\text{Et}_{4-n}\text{Pb}$, $n = 0-4$) degrade during combustion and further in the environment to produce a series of ionic compounds [176–178]. Speciation analysis is based on GC or HPLC with spectrometric detection [179,180].

33.4.1 Instrumental approaches

Gas chromatography based techniques

As only TAL compounds can be readily gas chromatographed, the ionic species must be derivatized prior to GC. The derivatization techniques include propylation [181–184] and butylation [182,185–188] using Grignard reagents and ethylation with NaBEt_4 [189,190]. Packed columns usually filled with Chromosorb W containing a 3–10% loading of OV-101 or Carbowax which had been used until recently [179] are being replaced by capillary columns with polymethoxysilane coatings (DB-1, HP-1, RSL-150) [180]. Packed columns do not allow for effective resolution between $\text{Me}_2\text{Pb}^{2+}$ and Et_3Pb^+ when butylation is used as the derivatization technique. The most widely used detection technique is QF AAS which offers DLs down to a few pg [179,191,192]. Gas chromatography–GF AAS remains inferior to GC–QF AAS in terms of both sensitivity and ease of operation. The DL reported was 8 pg (as Pb) for Me_4Pb and was rapidly degraded for higher boiling species [193,194]. Signal discrimination with the decreasing volatility of analytes is common to all the systems. Helium atmospheric pressure MIP AES offers detection limits in the sub-pg or low pg range [182,195,196]. Mass spectrometry with either electron ionization [197] or ICP [198] impact has been reported to offer an ADL at the 1 pg level.

Liquid chromatography based techniques

These offer a possibility to avoid the time consuming and interference prone derivatization step. Organoleads are separated as native species [199–202], APDC compounds [203,204] or ion pairs with pentane sulphonate [205,206] by means of reversed-phase [205,206], cation-exchange [200,202] or size exclusion chromatography [199]. Liquid chromatography–AAS couplings based on thermospray microatomization [203] and postcolumn ethylation [204] have been described. Liquid chromatography–direct injection nebulization ICP MS is the most efficient [205,206]. Absolute detection limits down to 0.2 pg (as Pb) have been reported [205].

33.4.2 Analysis of real samples

Standards

Only a few organolead compounds, Me_3PbCl , Et_3PbCl , Me_4Pb and Et_4Pb , are commercially available for use as standards. The synthesis of Me_2PbCl_2 and Et_2PbCl_2 has been described in the literature [166, 207]. Mixed methylethyl ionic compounds were identified in some samples by prediction of retention times of the derivatized species using the Kovat's retention index or on the basis of retention times of tetraalkyllead standards. Quantification of the mixed compounds is made by interpolation using the available standards. The preparation of propylated and butylated di- and trialkyllead standards is described elsewhere [182].

Environmental samples

Ionic alkyllead species are usually extracted from water as diethyldithiocarbamates into an organic solvent and then propylated or butylated with a Grignard reagent [181,182,207,208]. For the analysis of less polluted samples by AAS large volumes (up to 10 l) were found to be necessary [187] whereas a 100-ml sample is sufficient for GC–AES [181,182]. An enrichment step, e.g. by evaporation of the extract before derivatization, is needed unless a large volume injection technique is used [181]. Recoveries are usually quantitative but for unfiltered samples adsorption losses on particulate matter may account for up to 20% of the tetraalkyllead present [185].

Alkyllead compounds are not involved in mineralogical processes so complete matrix decomposition is not necessary. Separation of organolead from sediments and soils is exclusively based on solvent

TABLE 33.1

Speciation analysis for organolead in water and environmental matrices

Analyte	Separation/ preconcentration	Derivatization	Analytical technique	Application [Ref.]
IAL	extrn. with DDTC (pentane), rotary evaporation, dissoln. in nonane	butylation	GC-QF AAS	potable [187], rain, river, lake water, snow [210], soil [187]
IAL, TAL	extrn. with DDTC (benzene), rotary evaporation	butylation	GC-QF AAS	river water [188], river sediment [188, 207]
IAL, TAL	extrn. with DDTC (hexane)	propylation [181-183,208], butylation [182,185,208]	GC-QF AAS [183, 185], GC-MIP AES [181,182,211]	drainage [185], tap [181,182], rain water [182, 183], polar snow [211], road dust, soil, sediments [207], aerosol [183]
IAL	extrn. with DDTC, DMTC, APDC (hexane), precon- centration under stream of N ₂	butylation, phenylation	GC-QF AAS	soil, street dust [212]
IAL	extrn. with DMDTC	none	HPLC-QF AAS	water, soil, sediment [203]

IAL— Me₂Pb²⁺, Et₂Pb²⁺, Me₃Pb⁺, Et₃Pb⁺, MeEtPb²⁺, Me₂EtPb⁺, MeEt₂Pb⁺; TAL — Me_nEt_{4-n}Pb (*n* = 0-4).

extraction, usually with hexane. For extraction of IAL compounds a complexing agent, usually DDTC, is needed. EDTA is often added as an aid to disperse the sediment in a suspension and to facilitate the phase separation. Sodium benzoate was reported to increase the recoveries of the IAL species [207]. Satisfactory yields are usually obtained for tetraalkyllead and trialkyllead species but not for dialkyllead [209]. Selected procedures for speciation analysis for organolead in environmental waters, dust and sediments are summarized in Table 33.1.

Biological tissues

Since organolead compounds may be incorporated in the tissue, solubilization or decomposition of biological materials prior to separa-

TABLE 33.2

Speciation analysis for organolead in biological materials

Analyte	Sample preparation	Separation/ preconcentration, derivatization	Analytical technique	Application [Ref.]
IAL, TAL	TMAH hydrolysis (60°C; 1–2 h)	extrn. with DDTC (benzene), butylation	GC QF AAS	fish, clams, macrophytes [188,207]
Me ₃ Pb ⁺	haemolysis by freezing	extrn. with DDTC (pentane), butylation	GC GF AAS	blood [194]
TAL, IAL	enzymatic hydrolysis (37°C; 24–48 h)	extrn. with dithizone (hexane), butylation	GC QF AAS	snails[214], birds organs and eggs [213,214,216] fish, shrimp, scallop [192]
IAL	pulverization in liquid N ₂ , TMAH hydrolysis (room temperature; 2 h)	extrn. with DDTC (pentane), rotary evapn., dissoln. in nonane, butylation	GC QF AAS	grass, tree and shrub leaves [209]
Protein bound Pb	haemolysis by freezing, centrifugation	none	HPLC ICP MS	human and rat blood [199]

IAL— Me₂Pb²⁺, Et₂Pb²⁺, Me₃Pb⁺, Et₃Pb⁺, MeEtPb²⁺, Me₂EtPb⁺, MeEt₂Pb⁺; TAL — Me_nEt_{4-n}Pb (*n* = 0–4).

tion of the analytes is necessary. The sample is usually digested with TMAH [188,207,209] or hydrolyzed enzymatically with a mixture of lipase and protease [191,212–214]. Speciation of lead in seafoods has been discussed [215]. Methods for the analysis of biological materials are summarized in Table 33.2.

Accuracy considerations

Preservation of TAL in their authentic state is affected by sorbtion onto glass walls [184] and decomposition on the active sites. Ionic alkyllead species are not adsorbed to an appreciable extent [184]. Organolead compounds are known to decompose in solution in a light-

induced process promoted by microorganisms, suspended solids and various impurities [184,217]. Tetraalkyllead species are the least stable and degrade completely within few days [184,187]. Generally, no noticeable change of the IAL species in water samples stored in glass bottles at 4°C in the dark was observed for a period of up to 1–3 months [184,187]. The rate of decomposition dramatically depends on the origin of the sample and very little is known on the stability of dilute solutions (below 10 ng l⁻¹). To avoid volatilization of tetraalkyllead, samples should be stored frozen.

Airborne contamination starts affecting the analysis at the levels below 0.1 pg g⁻¹. Analytical procedure blanks of 20–30 fg g⁻¹ are common unless samples are not handled in clean bench cabinets [211]. Reagent impurities are removed by pre-extraction. A limiting factor is the purity of Grignard reagents which are not purifiable owing to the low stability; PrMgCl was found to be the best choice in this respect [181].

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Lithium

Lithium (atomic weight 6.941, melting point 181°C, $d = 0.53 \text{ g cm}^{-3}$) is a silvery-white highly reactive metal. It occurs in the earth's crust with the average abundance of 65 ppm. Lithium is an alkali metal but the small ion-size and hence the large charge density make it resemble alkaline earths in properties rather than alkali metals. Lithium is readily oxidized by air and reacts rapidly with water but the least vigorously of all the alkali metals. The hydroxide formed, LiOH, has basic strength comparable with that of $\text{Ba}(\text{OH})_2$. Lithium exists in solution as the Li^+ cation, unable to form complexes with inorganic ligands but, contrary to other alkali metals, able to form chelates, e.g. with azo compounds. Lithium can be precipitated as carbonate, fluoride or phosphate from alkaline solutions. Lithium nitrate and halides (except LiF) are deliquescent and soluble in polar organic solvents.

34.1 SEPARATION AND PRECONCENTRATION

Extraction

The crown-4 compounds with 14- and 15-member rings show high selectivity towards Li [1–4]. The extractability of the complex formed into an organic solvent is achieved by the formation of an intermolecular ion-pair with a counter anion (e.g. picrate) or of an intramolecular ion pair. Maximum extraction efficiency is observed at pH 10–11 with polar organic solvents. The extraction is fast enough to be automated in an FI system [3]. The extraction of the Li poly(oxyethylene)alkyl-phenylether (Triton X-100) with picrate has been studied [5]. 4-Acyl-5-pyrazolones with bulky substituents allow for effective synergic solvent extraction of Li in the presence of TOPO into non-polar solvents [6,7].

The Li isotopes were reported to be differentiated by extraction to give separation coefficients of 1.0032–1.020 [8]. Extraction of Li with benzoyltrifluoroacetone and TBA into CCl_4 has been reported [9].

Other methods

The small ion size and large charge density make the Li^+ cation easy to separate from other elements on cation-exchangers [10–12]. An enrichment of ^6Li vs ^7Li upon cation exchange [13] or extraction chromatography [14] has been reported. Lithium can be preconcentrated and separated from Na^+ on a lipophilic 14-crown-4 nitrophenol derivative loaded liquid membrane [15].

34.2 DETERMINATION TECHNIQUES

Spectrophotometry

Extraction with crown ethers is the basis of a steadily increasing number of spectrophotometric methods for Li. Chromogeneity of the extracted ion pair can be achieved by the presence of a chromogenic group in the ether itself [2,3] or a suitable counter-ion (e.g. picrate). Lithium is the only alkali metal that gives colour reactions with azodyes having either an $-\text{AsO}(\text{OH})_2$ or a $-\text{PO}(\text{OH})_2$ group in the *ortho* position to the azo group, such as, e.g. Thoron I [16]. Sodium may interfere to some extent and the results need to be corrected for its concentration in the sample.

Flame atomic absorption spectrometry

Flame AAS offers a DL of ca $0.1 \mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 , oxidizing (lean, blue) flame at the most sensitive 670.8 nm line. The strong suppression of the Li signal by Na, Ca and Mg can be alleviated by matrix modification with KH_2PO_4 [17]. Use of an N_2O – C_2H_2 flame instead of an air– C_2H_2 flame was recommended to minimize chemical interferences in the Li determination [18].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a sub-pg ADL but is plagued by volatilization losses of LiCl prior to atomization. Matrix modification with NH_4NO_3 [19] or its mixture with KH_2PO_4 [20] was recommended to increase the maximum permissible charring temperature to 1200°C [20]. The contribution of phosphate to non-specific background absor-

bance is a side effect [21]. The addition of H_2 to the Ar purge gas was reported to remove interferences due to the remaining residue and to make the direct calibration with aqueous standards possible [20]. The use of a red filter which absorbs radiation below 650 nm was recommended [21]. Another problem is the signal suppression and peak tailing associated with the formation of lithium carbide. As a remedy, tantalum carbide coated tubes have been proposed [22] and a procedure of *in-situ* tube-coating has been developed [23]. Slurry sampling GF AAS of molybdenum oxide using a tungsten atomizer was reported to offer a DL of 2 ng g^{-1} [24]. The relationship of the absorption of ^6Li and ^7Li hollow cathode lamp emissions was used to determine the Li isotopic composition by GF AAS at natural abundance levels [25].

Atomic emission spectrometry

Flame AES offers a DL of 0.04 ng ml^{-1} in C_2H_2 -air flame at the 670.8-nm line [27,28]. The background emission caused by organic matter and the high concentration of other elements found can be minimized by using an N_2O - C_2H_2 flame, working with small spectral bandwidth and using a two- or three-wavelength correction or derivative spectrometry [29]. Automated flame photometer was developed [30]. The use of Pt-loop atomizer was recommended for the suppression of CaOH and SrO emission [31]. Electrothermal AES using a tungsten atomizer was reported to offer an ADL of 0.04–0.5 pg [32,33]. Plasma source AES offers poorer sensitivity than FAES because of the decreased population of the Li atoms in a hotter environment [32]. A strong dependence of the stability [34,35] and intensity [36] of the ICP AES signal on the observation height above the torch coil was emphasized. No interferences were noted except that a high concentration of Na was found to enhance Li signal at low observation heights [34,35]. Use of MIP AES [36] and DCP AES [37] was reported.

Mass spectrometry

Lithium has two naturally occurring isotopes ^6Li and ^7Li with relative abundances of 6.43% and 93.57%, respectively, and thus is amenable to TI MS [11,12]. Because of the large isotopic fractionation during the Li^+ ion determination, $Li_2BO_2^+$ ions obtained from $Li_2B_4O_7$ are preferably monitored (at masses 56 and 57). To avoid the isobaric interference from Fe ion exchange separation is recommended [11]. For ICP MS, a DL of 0.03 ng ml^{-1} for Li was reported [38,39]. Polyatomic and isobaric interferences are absent [10,40]. Signal suppression by

high Na^+ concentration must be either avoided (e.g. by at least partial removal of Na [10]) or corrected for (by using an internal standard). As the latter, ^9Be which has a comparable mass with the analyte was used [40]. Memory effects were alleviated by rinsing with dilute HNO_3 for a few minutes [40]. Owing to the large mass difference between the isotopes ICP MS is quite sufficient for the accurate determination of the $^6\text{Li}/^7\text{Li}$ ratio [10].

Other techniques

The determination of lithium by NAA is severely jeopardized by the significant isotope effects due to the low relative atomic mass of lithium. The determination is based on measuring the tritium activity induced by the $^6\text{Li}(n,\alpha)^3\text{H}$ reaction and requires special facilities [41]. Lithium cannot be determined by X-ray fluorescence spectrometry. ICP AFS was reported to offer a DL of 0.3 ng ml^{-1} [42,43].

34.3 ANALYSIS OF REAL SAMPLES

Waters

Lithium is classified as an environmentally non-essential element and is employed as tracer of the water flow in open channels or pipes. The relatively low DLs of instrumental techniques for Li enable direct determination of this element (usually after acidification). The determination techniques used have included FAAS for raw and waste waters [18], ICP AES for mine and reference water [43] and GF AES for potable waters [33]. Cation-exchange separation of Li prior to the determination of its isotopes in sea water has been recommended [11].

Clinical materials

Clinical aspects of lithium have been discussed [44,45]. Serum and blood were analyzed directly upon dilution with H_2O [29], HNO_3 [40], and Triton X-100 [17,21,23,46–48], sometimes with addition of HNO_3 [21,48]. Heparin can be added as anticoagulant [48]. Serum samples are sometimes deproteinized with 10% HNO_3 [21]. The sensitivities of spectrophotometry (on extraction) and FAAS match the Li levels in the blood of treated patients, but are insufficient for measuring the normal blood Li levels. Flame ($\text{N}_2\text{O}-\text{C}_2\text{H}_2$) AES is sufficiently sensitive for direct analysis (DL $0.01\text{--}0.1 \text{ ng ml}^{-1}$) but requires relatively large volumes of samples and further information about the approximate Na

and K contents that suppress ionization. A microprocessor-controlled flame photometer has been developed for the automated analysis of serum, urine and plasma [30]. Graphite furnace AAS is sufficiently sensitive but matrix-matched standards are required for the analysis of serum and erythrocytes. When aqueous standards are used efficient background correction technique is mandatory [29]. The signal suppression by calcium and phosphate makes the calibration by standard additions necessary [21]. ICP MS not only offers a low detection limit (0.03 ng ml^{-1}) for Li in serum [38] but also enables isotopic analysis [10]. Digestion is required for serum and blood if ion exchange separation is incorporated [10]. For urine, the removal of organic matrix prior to dual cation-anion exchange was to be found not necessary; a dilution with 5% HNO_3 was sufficient [6].

Biological materials

Dry ashing is inappropriate because of severe volatilization losses of Li. Wet digestion with a mixture of HNO_3 - H_2O_2 [28], HNO_3 - H_2SO_4 [27] and HNO_3 (microwave-assisted) [40] has been proposed. Both direct nebulization and wet digestion with a HNO_3 - H_2SO_4 mixture were found satisfactory for the determination of Li in wine. The former method was recommended as the simplest [49].

Geological, industrial and other materials

In cosmochemistry and nuclear fusion technology deficiency of the ^6Li is used to estimate the amount of tritium produced by the $^6\text{Li}(\text{n},\alpha)^3\text{H}$ reaction. Lithium is readily leached from rocks and some soils but digestion with HF - HNO_3 - HClO_4 is recommended for total Li determination. Fusion is prone to error owing to volatilization losses of Li at 500°C . Furthermore, Li-free fluxes are hardly available. Greases were analyzed for Li by FAAS after pressure decomposition with HNO_3 - H_2SO_4 or dissolution in toluene-methanol [50]. Dissolution in acid mixture is preferred for coal, ash and glasses prior to the determination by emission techniques [34,35].

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Manganese

Manganese (Mn, atomic weight 54.94, melting point 1244°C, $d = 7.3 \text{ g cm}^{-3}$) is a white-grey, hard, brittle metal. It is fairly abundant in the earth's crust (*ca* 0.1%) where it occurs primarily as pyrolusite (MnO_2), in Fe ores and in deep sea nodules. The metal dissolves in dilute mineral acids with formation of Mn(II). Oxidation states of Mn from II to VII are known, the most popular being II, IV, VI and VII. The only common cation is Mn^{2+} (pale pink). Sodium hydroxide precipitates Mn(OH)_2 which is insoluble in excess of the reagent and is rapidly oxidized to the brown-black MnO_2aq . Manganese(II) forms many labile complexes, e.g. with EDTA, tartrate, cyanide. Strong oxidants (e.g. IO_4^-) oxidize Mn(II) in acidic solution to the violet permanganate, MnO_4^- , that is a strong oxidant. Manganese in oxidation states higher than II can be reduced to Mn(II) by boiling with concentrated HCl. Manganate (MnO_4^{2-}) is stable in strongly alkaline solution; otherwise it disproportionates into Mn(VII) and Mn(IV). The most widely used organomanganese compounds include ethylenedisithiocarbamate (used as fungicide) and methylcyclopentadienyl tricarbonyl (used as antiknock agent). Manganese is a biologically essential trace element and a constituent of many enzymes. In higher concentrations it is toxic. The environmental occurrence of Mn can be either natural (erosion of rocks) or anthropogenic, mostly as a result of mining and metallurgy [1].

35.1 SEPARATION AND PRECONCENTRATION

Extraction

Manganese can be extracted at pH 6–8 as the dithiocarbamate into a variety of solvents (e.g. CHCl_3 , CCl_4 or Freon TF) and then stripped

into HNO_3 [2]. Extraction of Mn salicylate with liquid anion [3,4] or chelating exchangers [5] into non polar solvents followed by stripping into dilute acids was reported. The Mn-TTA complex could be fairly selectively extracted from a complex matrix (Cu, Fe, Pb, Zn, Al) as the ion-pair with TBA (MIBK) in the presence of thiosulphate and sulphosalicylate [6] or as the ion-pair with DB-18-crown-6 (*o*-dichlorobenzene) (pH 3) [7]. Extraction of Mn with *bis*-2-ethylhexylphosphoric acid (kerosene) has been reported [8].

Other techniques

Coprecipitation of Mn(II) with APDC (with Co(II) as carrier) or with 8-quinolinol (with Mg as carrier) has been used [9]. Colloidal Mn(III)/Mn(IV) oxides coprecipitate with the same yield as Mn(II) [9]. *On-line* electrodeposition of Mn (both anodic and cathodic) was found to be successful [10]. *On-line* sorption on the immobilized 8-hydroxyquinoline has been reported [11].

35.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometric determination of Mn has been reviewed [12]. Oxidation of Mn(II) to MnO_4^- by powerful oxidants ($\text{S}_2\text{O}_8^{2-}$, Ce(IV), BiO_3^- , IO_4^-) in acidic solutions, often in the presence of Ag^+ or Co^{2+} as catalysts, forms the basis of a poorly sensitive ($\epsilon = 2.4 \times 10^3$ at 528 nm) but very selective method, especially if derivative spectra processing is used [13]. A higher sensitivity ($\epsilon = 1.1 \times 10^4$ at 455 nm) is offered by the formaldoxime method [14,15] which gives appreciable selectivity in the presence of cyanide. The catalytic effect of Mn on the oxidation of some basic dyes [16–18], succinide dioxime [19] or 7,7,8,8-tetracyanoquinodimethane [11] (chemiluminescence) has been employed for the determination of Mn in various matrices, and also in FI mode.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.05 \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 , oxidizing (lean, blue) flame at the most sensitive 279.5 nm line [3,5,8]. The Mn signal is depressed by Si which can be overcome by the addition of CaCl_2 . Large excess of Fe ($>10 \text{ g l}^{-1}$) increases the Mn absorption. Water-organic emulsions diluted with kerosene can be analyzed [8].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of $ca\ 0.01\ \text{ng ml}^{-1}$ (characteristic mass 2 pg) at the 279.5 nm line using a pyrocoated tube and platform atomization with $\text{Mg}(\text{NO}_3)_2$ as matrix modifier. The less sensitive 403.1 nm line was used in the case of samples with elevated Mn contents [20,21]. Loss of Mn prior to atomization is the basic problem. Vaporization of Mn in a GF has been studied by a radiotracer (^{56}Mn) method [22]. Detailed studies of interferences of inorganic acids and salts [23] with particular emphasis on chloride has been reported [24]. The addition of EDTA helps to eliminate negative interference by Ca and Mg [25]. Without a modifier a pyrolysis temperature of 1100 °C can be used for Mn. To increase this temperature to 1400–1500 °C various modifiers including HNO_3 [20,26,27], $\text{Ca}^{2+}\text{--H}_3\text{PO}_4\text{--HNO}_3$ [23], $\text{Mg}(\text{NO}_3)_2\text{--}(\text{NH}_4)_2\text{HPO}_4$ [28,29], NaOH [30], ascorbic acid [24], thiourea [31], Pt [32] and Pd–Mg [33] have been proposed. The $\text{Ni}(\text{NO}_3)_2$ modifier was recommended to alleviate the interference from the $\text{NaNO}_3\text{--H}_3\text{BO}_3$ medium on fusion [34]. Slurry GF AAS analysis of single cell proteins [21] and other biological materials [20,29] has been developed.

Atomic emission spectrometry

ICP AES offers a DL of $ca\ 1\ \text{ng ml}^{-1}$ at the most sensitive 257.61 nm, 259.37 nm and 260.57 nm lines. The two latter lines are interfered with by high Fe concentrations. Mineral acids suppress the Mn signal and need to be compensated for, e.g. by real-time internal standardization with Sc [35]. Other sources for AES included a magnetically altered thin-film plasma [36] and a dual cathode discharge lamp [37].

Other techniques

Manganese is readily determined by XRF, usually in a multielement array [9]. Laser-excited ETA AFS offers an ADL of 0.1 pg which is contamination controlled to the 1 pg level [29]. Neutron activation of Mn yields ^{56}Mn ($t_{1/2} = 2.56\ \text{h}$, $E_\gamma = 0.845\ \text{MeV}$) of which γ -counting forms the basis of INAA. Iron interferes. Manganese has only one stable isotope ^{55}Mn which can be determined by ICP MS, usually in a multielement array.

35.3 ANALYSIS OF REAL SAMPLES

Manganese is often determined in many samples in a multielement array (*cf.* Part II). The concentrations of Mn in geological samples are

easily accessed by FAAS, especially after extraction of an Mn complex into MIBK [6] or spectrophotometry [13].

Environmental and geological samples

Occupational exposure for Mn in air was estimated by near-real-time electrostatic precipitation GF AAS with a DL of 0.05 ng/m^3 [38]. The concentration of Mn in environmental waters is estimated to be $10\text{--}100 \text{ ng l}^{-1}$ [1]. Shipboard analyses by an FI chemiluminescence system [11] or using a photometric submersible analyzer for *in-situ* analysis have been reported [39]. Albeit direct GF AAS of sea [30,32] and lake [26] water is apparently feasible, preconcentration of Mn commonly precedes water analyses (*cf.* Table 35.1). Sediment cores should be handled in an inert atmosphere to avoid oxidation, e.g. Fe(II) present may oxidize to Fe(III) and precipitate as Fe(OH)_3 carrying trace Mn by coprecipitation [9].

Clinical materials

Contamination hazard is pertinent. Any labware as well as the environment itself are potential sources of Mn. Class-100 clean room facilities are required [2,29,42,43]. Plastic needles and cannulas cleaned by sequential leaching with HCl (1+1) and HNO_3 (1+1) [2] should be used for blood sampling. The first few millilitres of sample should be discarded [44]. Attention must be paid to the possible presence of Mn in the anticoagulants used. Problems encountered during handling of serum samples have been discussed [45]. For storage at 5°C up to 7 d no significant changes were noted. For medium- and long-term storage freezing of the samples at -22°C is advised [46]. The normal range of serum Mn is $0.4\text{--}1.0 \text{ ng ml}^{-1}$ [47]. In blood, Mn is concentrated in erythrocytes [47–49] being bound to β -globulin or transferrin [47]. Determination of Mn has been reviewed [46] with special emphasis on GF AAS [44,50,51] which is definitely the most widely used technique. Direct analysis of serum on 1+1 dilution with Triton X-100 using a pyrolytically coated tube with platform atomization and Zeeman background correction is recommended [25,43,47]. Matrix modifiers, e.g. HNO_3 [21] or $\text{Mg(NO}_3)_2$ [48], were used for blood analysis. Deproteinization with HNO_3 was used to avoid problems with the carbonaceous residues [42] but in the case of blood it may cause losses since Mn is bound to haem which coprecipitates [52]. Low temperature ashing [27] or digestion with $\text{HNO}_3\text{--H}_2\text{O}_2$ [48] are better choices for whole blood. Calibration by standard additions is generally indispensable despite

TABLE 35.1

Methods for the determination of Mn in water

Water sample (amount)	Separation and/or preconcentration	Determin. technique	DL (ng/l)	Ref.
Tap (5 ml), mineral (0.25 ml)	<i>on-line</i> electrodeposition	GF AAS	10–30 ^a	10
Sea (0.35 l)	extraction with APDC/DDTC (Freon TF); back-extraction (HNO ₃)	GF AAS	5	2
Sea	<i>on-line</i> sorption on immobilized 8-hydroxyquinoline	CL	5	11
Tap, river (0.3 l)	coprecipitation as 8-hydroxyquinoline complex with Mg carrier	GF AAS	14	40
Ground, river, lake, sea, tap (0.1 l), waste (1 ml)	extraction with DDTC (DIBK)	LEI	0.1	41
Natural (10 ml)	extraction with TTA and DB-18-crown-6 (<i>o</i> -dichlorobenzene), back-extraction (H ₂ O)	FAAS	n.g.	7
Marine sediment pore (0.1 ml)	UV irradiation, coprecipitation as APDC complex with Co carrier	XRF	50	9

^a Absolute detection limit, in pg.

the use of the Zeeman correction [25]. A protocol for the accuracy evaluation for the determination of Mn in blood by AAS has been developed [53]. Radiochemical NAA is an excellent method to determine Mn in plasma and serum as after completion of activation it becomes totally insensitive to external Mn addition [45]. For the determination of Mn in urine, use of the L'vov platform and the Mg(NO₃)₂ matrix modifier ensure the best performance [46]. For hair samples sequential washings with non-ionic detergent (e.g. Triton X-100), water, ethanol and again with water have been recommended [44].

Plant and animal tissues

Plants may contain 1–700 ppm of Mn and can be analyzed on digestion by GF AAS [29] or on extraction preconcentration by FAAS [3,5]. Direct Mn determination in biosamples by ETA AAS using an Mo

tube atomizer with thiourea matrix modifier offered an ADL of 0.9 pg [31] Homogenization of tissue samples with water followed by HCl leaching was used for the determination of Mn in rat liver by FAAS [54].

Speciation

Methylcyclopentadienylmanganese tricarbonyl, pentamethylcyclopentadienylmanganese tricarbonyl and cyclopentadienylmanganese tricarbonyl (cymanterene) were determined in gasoline by packed column GC with FPD with a DL of $0.6 \mu\text{g g}^{-1}$ [55]. Cymantrene, methylcyclopentadienylmanganese tricarbonyl, hydroxycyclopentadiene–manganese tricarbonyl and carboxycyclopentadienemanganese tricarbonyl in rat urine were separated by reverse-phase HPLC and gradient eluted with a Tris buffer to ICP MS [56].

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Mercury

Mercury (Hg, atomic weight 200.59, melting point -38.9°C , boiling point 356.9°C , $d = 13.55 \text{ g cm}^{-3}$) is a silvery metal, liquid at room temperature. It occurs in the earth's crust with an average abundance of 0.05 ppm, primarily as cinnabar (HgS). It is a highly toxic element and the large-scale production, uses (mostly in chloralkali and electrical industries) and release from the fossil fuels combustion give rise to serious environmental concerns. Organomercury compounds, widely used as biocides in the 1960s, have been almost entirely banned in the developed countries because of their toxicity. Nevertheless, the uptake of neuro- and embryotoxic methylmercury and the extent of its natural formation in biota give rise to ecotoxicological concerns and prompt speciation analysis. Environmental and toxicological aspects of Hg were discussed [1].

Mercury dissolves in hot HNO_3 and hot H_2SO_4 to give Hg^{2+} . Cold HNO_3 reacts to form Hg(I) if an excess of the metal is present. Mercury dissolves Ag, Au, Na, Zn, Th and Pb to form amalgams, and reacts with S, Se and iodine. The metal exists in two oxidation states I and II, the latter being more stable. The almost unique dimeric Hg_2^{2+} disproportionates readily to Hg(II) and elemental mercury (Hg^0). Mercury(II) forms strong complexes with halides and sulphur donors. Many mercury compounds, e.g. HgCl_2 , are covalent but water soluble. The analytical chemistry of Hg was reviewed with particular emphasis on speciation [2,3].

36.1 SEPARATION AND PRECONCENTRATION

Volatilization of Hg^0 , usually applied in CF and FI systems, is the most widely used separation technique prior to atomic spectroscopy.

Relevant commercial systems are widely available. The use of NaBEt_4 to convert mercury into volatile species is becoming increasingly popular as it enables a simultaneous derivatization of organomercury compounds [4–9]. Extraction is preferred for spectrophotometry and RNAA. Coprecipitation and sorption are practically not used unless prior to determination of Hg in a multielement array (*cf.* Part II).

36.1.1 Volatilization

Reduction to elemental mercury

The most widely used reductants include SnCl_2 [10–31] and NaBH_4 [23,32–43], usually applied in acid media. Tin(II) chloride is capable of reducing only ionic mercury, unless it is used in an NaOH solution in the presence of $\text{K}_2\text{S}_2\text{O}_8$ [17,44] and catalysts such as e.g. Cd, Cu(II) [17,45] or Fe(II) [46]. It is preferred to NaBH_4 whenever the procedure involves an oxidative digestion and because of the lower blank contribution. The advantages of NaBH_4 include rapid reaction kinetics, lower susceptibility to interferences [47], applicability to slurries [48] and the ability to reduce organic Hg compounds to Hg^0 [49] (not all the compounds are reduced, however, to the same extent). Electrolytic reduction of Hg(II) using Cr(II) ions produced from Cr(III) in a flow-type cell has been reported [50]. The reduction of Hg(II) is interfered with by transition metals, such as Cu, Ni, Ag, Au, Pt and the hydride-forming elements [27], complexing agents, e.g. cysteine [49] and NO_x (formed during digestion with HNO_3) [51]. The interferences are less pronounced in alkaline media [52]. Interference from Se can be removed by its oxidation to Se(VI), e.g. with KMnO_4 [53]. Interferences by transition metals (Cu, Ni, Cd and Pb) were minimized in micellar media and interferences by hydride-forming elements were reduced by citrate buffer or dioctylsulphonosuccinate [42,43,54].

Separation

Separation of mercury vapour is usually carried out using some sort of open chamber in which the reaction products are separated by employing an inert purge gas (*cf.* Section 5.2.1). Three types of a gas–liquid separators have been compared for FI cold vapour generation and the relevant literature was reviewed [55]. The problems evoked include the moisture carry-over, resulting in gradual loss of the detector sensitivity and the baseline drift [54,56], and large dead volumes, leading to broader peaks and poorer detection limits. Chemical desic-

cants such as conc. H_2SO_4 , $\text{Mg}(\text{ClO}_4)_2$ or anhydrous CaCl_2 have been used but they become saturated fairly quickly and give rise to contamination and absorption losses. Physical moisture traps such as semipermeable Nafion drying tubes or microporous PTFE membranes were found to be more successful [54,55].

Preconcentration

Preconcentration of mercury vapour aimed at reversing the gas-phase dilution factor is usually done by trapping Hg as an amalgam on the surface of a noble metal gauze or gold-covered sand packed into a quartz tube. A comparison of various substrates showed Au to be the best suited gauze material [57]. Silver surfaces are often deactivated by sulphides and halides [58]. The trapped mercury is released to the detector by heating the trap; particularly advantageous is *in situ* deposition in a graphite furnace lined with Au [59], Pt [21,23], Pd [60] or Ir [61]. Sorption of mercury on a Au [31] or Au–Pt gauze [62] and direct revaporization into a graphite [62] or quartz [31] furnace are an alternative. Thermal desorption of Hg^0 and some organomercury compounds from a gold column has been studied in detail [63]. Precision and accuracy can be improved by a dual amalgamation technique in which the second trap constitutes a well characterized integral part of the analytical system [64].

36.1.2 Other methods

Mercury can be separated by extraction of HgI_2 and HgI_3^- into cyclohexane or aliphatic ketones from an acid medium [65]. In particular, extraction of HgI_2 is a very selective method of separating Hg. Mercury and organomercurials can be extracted with dithiocarbamates [66,67] and benzothiazole derivatives [68]. Extraction of the Hg dithizonate which allows the separation of Hg from Cu, Bi, Zn, Ni, Pb and Pd, and, under appropriate conditions, from Ag, usually precedes spectrophotometric determination.

36.2 DETERMINATION TECHNIQUES

The majority of methods are based on the introduction of the Hg^0 vapour into the atomizer of an atomic absorption, fluorescence or emission (MIP) spectrometer. Detection limits at the low pg level can be

obtained which are controlled by the blank rather than by the instrument characteristics [69]. Spectrophotometry is widely used because of its simplicity and field adaptability; the maturity of this technique is best illustrated by the virtual lack of publications in recent years.

Spectrophotometry

Spectrophotometry is based on the rapid reaction of Hg(II) (and methyl-, ethyl- and phenylmercury) with dithizone in acid medium to form the orange–yellow dithizonate which is extractable into CHCl_3 or CCl_4 ($\epsilon = 7.1 \times 10^4$ at 485 nm). Palladium interferes and must be removed by prior separation with dimethylglyoxime. Gold and Pt should be reduced prior to the extraction of Hg.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $4 \mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 oxidizing (lean, blue) flame at the most sensitive 253.7 nm line. Ascorbic acid, SnCl_2 or other reducing agents may reduce the mercury present to Hg(I) or Hg^0 leading to erroneously high results. Flame AAS is practically not used preference being given to quartz furnace AAS.

Quartz furnace atomic absorption spectrometry

Quartz furnace AAS is the most widely applied method for the determination of Hg. It offers an ADL in the low pg range which allows an approximate detection limit of 1 pg ml^{-1} in real samples to be obtained. Interferences are rare and include non-specific signals from CO, NO, or smoke [70] and chlorine [71] which can be eliminated by background correction or by using a separative column atomizer [70].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of 2 ng ml^{-1} and a characteristic mass of 0.1 ng. As all mercury compounds are extremely volatile, losses occur above 200°C even in the presence of modifiers. A two-step drying procedure, at 90 and 140°C , followed by atomization at 1000°C was recommended [72,73]. Palladium, obtained *in situ* by high temperature pyrolysis of $\text{Pd}(\text{NO}_3)_2$, was found to be the most efficient matrix modifier [66,72–76]. Pyrolysis temperatures of up to 400°C could be tolerated, however, only if the modifier was reduced prior to sample injection. Mercury is apparently stabilized not only by amalgamation but also by oxide formation [72]. A single addition of $15 \mu\text{g Pd}$ was sufficient for

40–60 determinations under normal operating conditions [74,76]. Cationic interferences are unlikely owing to the stability of the Pd–Hg compound [74]; chloride, sulphate, iodide and cyanide interfere by forming stable and volatile compounds in the condensed and/or gas phase [74,77]. The interference caused by high NaCl concentrations was eliminated by using a mixture of 95% Ar and 5% H₂ as the purge gas [74,76]. The low allowable pyrolysis temperatures are responsible for a very high matrix background which makes the use of the Zeeman correction [66,72,74,78] or matrix removal prior to analysis [66] mandatory. An elegant method is based on the *in-situ* preconcentration of Hg⁰ vapour in a noble-metal-lined graphite tube [21,23,60,61] or its electrodeposition on a Pt wire which is then inserted into a GF for direct measurement [79].

Atomic emission spectrometry

The most popular plasma for Hg determination is the MIP. It offers an ADL of 0.05 pg and can be used not only for the atomization of Hg⁰ vapour [11] but also for that of a GC effluent [80–85]. Different MIP cavities have been discussed [86]. Inductively coupled plasma AES offers a DL of 20–50 ng ml⁻¹ at the most sensitive 253.65 and 194.23 nm lines which can be improved by solvent extraction, also in FIA mode [87]. The 253.65 nm line is overlapped by Fe and Co. An ADL of ICP AES of 4 pg has been reported [88]. Despite its freedom from non-specific background absorption of volatile organic species ICP AES is seldom used, unless as a detector for GC [89]. Ring discharge AES with an amalgamation preconcentration step was reported to give a DL of 0.5 pg ml⁻¹ [12].

Fluorescence techniques

Non-dispersive AFS with atomization in an Ar–H₂ flame is a commercially available, cheap, highly selective and sensitive (ADL down to a few pg) determination technique for gaseous Hg [5,8,17,37,64,90–92]. Subpicogram ADLs are readily obtained. A filter fluorometer is generally sufficient; however, the linearity range may be too small [93]. The technique is readily applicable to FIA [37]. Atomization in an MIP has been proposed instead of flame [94]. Two-step ETA LE AFS has been developed offering an ADL of 90 fg [95].

Mass spectrometry

Mercury has seven stable isotopes ¹⁹⁶Hg (0.15%), ¹⁹⁸Hg (10.02%), ¹⁹⁹Hg (16.83%), ²⁰⁰Hg (23.13%), ²⁰¹Hg (13.22%), ²⁰²Hg (29.80%), ²⁰⁴Hg

(6.85%) and thus it is readily amenable to isotope dilution. The most abundant ^{202}Hg is usually the analyte nuclide whereas ^{199}Hg [34] and ^{201}Hg [29,96–98] are the most common spikes. Detection limits reported for ICP MS were 30 pg ml^{-1} with direct injection nebulization [99] and 2.4 ng ml^{-1} in FIA mode [97]. The sensitivity is increased by vapour introduction of Hg; an ADL of 8 pg has been reported [29,34]. Uses of ETV ICP MS [100] and ID SS MS [98] have been reported.

Neutron activation analysis

Neutron activation analysis is based on the reaction $^{202}\text{Hg}(\text{n},\gamma)^{203}\text{Hg}$ ($t_{1/2} = 46.6\text{ d}$, $E_\gamma = 0.279\text{ MeV}$, $E_\beta = 0.208\text{ MeV}$). The counted nuclide, ^{203}Hg , can also be produced by the $^{203}\text{Tl}(\text{n},\text{p})^{203}\text{Hg}$ and $^{206}\text{Pb}(\text{n},\alpha)^{203}\text{Hg}$ reactions; Tl and Pb interfere at higher than 100-fold excess. An alternative is the irradiation of ^{196}Hg (only 0.2% abundance but more easily activated) which leads to a mixture of ^{197}Hg ($t_{1/2} = 23\text{ h}$) and $^{197\text{m}}\text{Hg}$ ($t_{1/2} = 65\text{ h}$), both of which are γ -emitters at 77.3 keV with good counting statistics [101,102]. The γ -activity of ^{197}Hg is measured after its volatilization and trapping [16], or extraction [103,104].

36.3 ANALYSIS OF REAL SAMPLES FOR TOTAL MERCURY CONTENT

Determination of total mercury requires conversion of all the forms of Hg (including simple organomercurials and humic acids or protein-bound Hg) to Hg^{2+} . Whereas for biological and geochemical materials a common oxidative acid attack generally ensures the presence of all the mercury as Hg^{2+} in the resulting solution, customized approaches are usually necessary for water samples. The oxidative digestion step is followed by reduction of Hg^{2+} to Hg^0 and the determination of the latter, usually by CV AAS or AFS. Accuracy problems encountered in the vapour injection calibration method for the determination of Hg by amalgamation CV AAS have been discussed [105,106].

36.3.1 Environmental and geological materials

Air

The biogeochemical cycle of Hg involves a considerable flux from the marine environment to the atmosphere *via* sea–air partitioning [1,107, 108]. Mercury in the gaseous fraction consists of elemental Hg^0 and alkylmercury species; all the forms are collected from air on graphitized

carbon black [90], gold [91], PbS [109] or organic [110] sorbents. Air particulates are collected by filtration [111] or electrostatic precipitation [112]. Mercury species are thermally released either onto a GC column or directly to the detector for the total mercury determination. Detection limits of *ca* 1 ng/m³ by CV AAS are common [91]. Determination of Hg vapour in air using electrically heated, gold-coated wire loops, *in-torch* vaporization sample introduction ICP AES was proposed [113].

Water

Class 100 clean room conditions are required for Hg determination in sea, river, estuarine and rain water at picomolar levels [13]. The long-term stability of Hg in water has been exhaustively investigated [114,115]. Water should be collected in glass bottles, acidified to pH 2, frozen and stored in the dark; adsorption of Hg is further reduced by the addition of CaI₂. Digestion with HNO₃–H₂SO₄ with addition of KMnO₄ and K₂S₂O₈ [23,36,71] or Co(III) [116], applied in *on-line* [71,117] or microwave-assisted mode [117] was found to be efficient. Alternatively, photooxidation with HCl+HNO₃ mixture has been recommended [49, 115]. NaBH₄ appears to be the reducing agent of choice. For total Hg determinations below 10 ng l⁻¹, however, SnCl₂ is preferred because of a lower blank contribution [23]. Purification of reagents was achieved using an Hg-selective ion-exchange resin, Chelate S, resulting in blank levels below 1.5 ng l⁻¹ [23]. Analytical methods for the determination of total Hg in water are summarized in Table 36.1.

Geological samples

Cinnabar is often present in geological materials such as rocks, soils and sediments whereas organomercurials occur in soils and sediments implicated in mercury transformation and pollution [1,24]. Marine sediments have been analyzed by slurry GF AAS [75]. Cinnabar as well as organomercurials dissolve very slowly in HNO₃–H₂SO₄ at room temperature but rapidly on a boiling water bath allowing determination of total Hg in geomaterials [24]. To prevent the loss of mercury sample must be dried at a temperature as low as possible [15]. Digestion is the most critical step. An extensive comparison study of five digestion procedures of soils showed the necessity of a closed system at elevated temperatures, preferably heated with microwaves [15]. Lower results were obtained using decomposition in closed, but not hermetically sealed, silica tubes owing to the volatilization losses [27]. PTFE pressure bombs can absorb considerable amounts of mercury leading to

TABLE 36.1

Analytical methods for the determination of total mercury in water

Sample (amount)	Separation and/or preconcentration	Detection technique	DL (ng/l)	Ref.
Lake, river, mineral water (60 ml)	electrodeposition on Pt	GF AAS	40	79
Lake, rain water (50 ml)	reduction with SnCl_2 , amalgamation with Au	GF AAS	0.1	22
Lake water (50 ml)	reduction with SnCl_2 , amalgamation with Au	MIP AES	0.01	11
Water (200 ml)	reduction with SnCl_2 , amalgamation with Au	ID ICP MS	0.2	29
Sea, river water (100 ml)	reduction with SnCl_2 , amalgamation with Au	ring discharge ARS	0.5	12
Sea, estuarine, river, rain water (2 l)	reduction with SnCl_2 , amalgamation with Au	GF CV AAS	0.04	13
Sea, waste water (50 ml)	reduction with NaBH_4 , trapping on Pd-coated GF	GF CV AAS	0.6	60
Marsh water (100 ml)	digestion with HNO_3 – H_2SO_4 – KMnO_4 – $\text{K}_2\text{S}_2\text{O}_8$; redn. with SnCl_2 in H_2SO_4 or NaBH_4 in NaOH , trapping on Pt in GF	GF CV AAS	n.g.	23
Lake, river	reduction with NaBH_4	ID ICP MS	8 ^a	34
Wastewater	reduction with NaBH_4 after oxidation of organoHg with $\text{S}_2\text{O}_8^{2-}$ in the presence of Cd^{2+}	CV AAS	150	36
Water	reduction with SnCl_2	FI CV AFS	180	26
Wastewater	reduction with SnCl_2 in NaOH in the presence of Cu(II) and $\text{K}_2\text{S}_2\text{O}_8$	CV AAS	100	17

^a Absolute detection limit, pg.

losses and memory effects. For total Hg determination MeHg has been decomposed by UV irradiation or by digestion with HNO_3 – HClO_4 [16]. Analytical methods for the determination of total mercury in geological samples are summarized in Table 36.2.

TABLE 36.2

Determination of total mercury in geological materials

Sample (amount)	Decomposition	Reduction	Separation	Detection technique	Ref.
CRMs (1–4 g)	HNO ₃ –H ₂ SO ₄	SnCl ₂	volatilization as Hg ⁰	QF AAS	24
CRMs (0.5 g)	<i>aqua regia</i> (bomb)	NaBH ₄	volatilization as hydride	FI ND AFS	37
CRMs (<0.5 g)	HNO ₃ –HCl (bomb)	SnCl ₂	amalgamation with Au	QF AAS	27
CRMs (0.2 g)	HNO ₃ –HCl (microwave assisted)	NaBH ₄		ICP MS	34
Soils, sediments	HNO ₃ –HClO ₄ – HCl	SnCl ₂	amalgamation with Au	QF AAS	16
Soils, sediments	pyrolysis– volatilization		trapping by formation of HgSe	RNAA	16
Soils (0.5 g)	HNO ₃ (microwave assisted)	SnCl ₂ – NH ₂ OH	volatilization as Hg ⁰	QF AAS	15
Soils	HNO ₃ –H ₂ SO ₄	SnCl ₂	volatilization as Hg ⁰	AAS	30
Sediments (0.5 g)	HF–HNO ₃ – HClO ₄	SnCl ₂	amalgamation with Au	GF AAS	22

36.3.2 Biological materials

Contamination is the major problem in clinical analysis. Samples must be sealed in quartz containers or (when in polyethylene) stored in hermetically closed and impermeable boxes to prevent Hg uptake from air [101]. The gaseous part of the mercury in the air is not retained by the HEPA filters [101]. Collection tube requires precautions to avoid contamination and to prevent volatilization and loss of Hg vapour. Blood is conveniently collected, stored, and transported in a heparanized

Vacutainer®. Urine should be acidified. Drying by lyophilization (at -5°C for 6 h) produced a 1% loss of Hg [38].

Direct analysis of blood and plasma by GF AAS is difficult because of losses at the pyrolysis stage and large unspecific background [78]. Digestion is necessary, usually with a strongly oxidizing mixture, whereas CV AAS is the most widely used technique. The main problem in the sample digestion for Hg is its volatility and mobility. Various official methods are based on the oxidative digestion with mixtures of concentrated acids (HNO_3 , H_2SO_4 , HClO_4) under reflux [25]. A critical comparison for biological and environmental samples showed HNO_3 – H_2SO_4 to be the most suitable [30]. The recoveries of the organic mercury from fish and kidney by the use of HNO_3 only and HNO_3 – HClO_4 were very low although quantitative recoveries for inorganic Hg were obtained [30]. The digestion method based on the oxidation with saturated solution of dichromate in dilute H_2SO_4 medium was satisfactory [25]. A cold (at -10°C) mineralization procedure (HNO_3 – H_2SO_4 – HClO_4 – KMnO_4 , H_2O_2) has been developed [33,38]. High pressure bomb digestion with HNO_3 [33,118] (also microwave-assisted) of fish tissue is apparently more efficient than the traditional open vessel method [20,35,39]. *On-line* microwave digestion of blood with KBr – KBrO_3 – KMnO_4 has been proposed [41]. Bromate–bromide or KMnO_4 together with NaBH_4 is effective in decomposing most of the organic mercury compounds in urine; adsorption of MnO_2 on vessel walls is prevented by the addition of NH_2OH or in FI mode owing to the short residence time of the reaction mixture in the system [40].

Interlaboratory surveys of the determination of total mercury in hair [119] and cod muscle [96] have been presented. A protocol for the preparation and characterization of a bovine blood containing intrinsic and elevated levels of Hg has been proposed [120]. Analytical methods for the determination of Hg in biological tissues are summarized in Table 36.3.

36.3.3 Industrial materials

Dissolution of solid and liquid fuels in a special device for burning organic substances has been developed [122]. Solid fuels can be decomposed with a mixture of HNO_3 , HF and H_2SO_4 in PTFE bombs in the presence of NH_4VO_3 that acts as an oxidation catalyst [123]. Pyrolysis was recommended as a method of separating Hg from industrial samples of complex composition, for some samples appropriate additives

TABLE 36.3

Determination of total mercury in biological materials

Sample (amount)	Decomposition	Reduction	Separation/preconcentration	Detection technique	DL (ng/ml)	Ref.
Serum, blood	HNO ₃ –H ₂ SO ₄ –HClO ₄ ; oxidn. with (NH ₄) ₂ S ₂ O ₈	none	extrn. with Ni-DDTC (CHCl ₃)	RNAA	n.g.	101
Serum (0.1 g), CRMs	HNO ₃ (bomb)	SnCl ₂	amalgamation with Au	QF AAS	0.1 ^a	18
Blood (1–1.5 ml)	dil. HCl		extrn. with DDTC (toluene); back-extrn. (HCl)	GF AAS	2	66
Blood, urine, fish	(bomb micro-wave)	NaBH ₄	volatn. as Hg ⁰	QF AAS	0.05 (0.16 ^a)	117
Hair	HNO ₃ (bomb or quartz ampoule)	SnCl ₂	Au–Pt grid	QF AAS	100 ^b	121
Hair, fish, mussels, placenta, CRMs	HNO ₃ –HClO ₄ –HCl	SnCl ₂	gold amalgamation	QF AAS	n.g.	16
Hair, fish, mussels, placenta, CRMs	pyrolysis–volatn.		trapping by formation of HgSe	NAA	n.g.	16
Hair, urine, CRMs (10 ml or 100 mg)	HNO ₃ (microwave assisted)	SnCl ₂		QF AFS	0.9 ng/l	28
Urine (0.5 ml)	KBr/KBrO ₃ , KMnO ₄	NaBH ₄	volatn. as Hg ⁰	FIA QF AAS	0.1	40
Fish (0.2 g)	HNO ₃ (microwave assisted)	NaBH ₄	volatn. as Hg ⁰	QF AAS	n.g.	39
Fish, shrimp, mussels (0.2–0.5 g)	HNO ₃ –H ₂ SO ₄ –HClO ₄ –KMnO ₄ , H ₂ O ₂ (cold) or HNO ₃ (bomb)	NaBH ₄	volatn. as Hg ⁰	QF AAS	n.g.	33

continued

TABLE 36.3 (continuation)

Sample (amount)	Decomposition	Reduction	Separation/preconcentration	Detection technique	DL (ng/ml)	Ref.
Fish, molluscs, crustaceans	HNO ₃ –H ₂ SO ₄ –HClO ₄ –KMnO ₄ –H ₂ O ₂	NaBH ₄	volatn. as Hg ⁰	QF AAS	0.05	38
Fish, lobster, scallop (1 g)	HNO ₃ (bomb)	SnCl ₂	volatn. as Hg ⁰	QF AAS	n.g.	10
Fish (0.2 g)	HNO ₃ (microwave)	NaBH ₄	volatn. as Hg ⁰	QF AAS	0.2	39
Fish (1 g), leaves (1–3 g), urine	combustion with O ₂ , cryotrapping		copptn. with Ag ₂ S	ID SSMS	n.g.	98
Fish, animal tissue (0.1–3 g)	HNO ₃ –H ₂ SO ₄	SnCl ₂		QF AAS	n.g.	30
Mussels (0.5 g)	HNO ₃	SnCl ₂	amalgamation with Au	GF AAS	0.005 ^a	22
CRM plant (0.5 g)	K ₂ Cr ₂ O ₇ in dil. H ₂ SO ₄	SnCl ₂		QF AAS	3 ^a	25
CRMs (50–70 mg)			extrn. with ethylacetate (CHCl ₃)	RNAA	140	104
CRMs (100 mg)	HNO ₃ (microwave assisted)	SnCl ₂	volatn. as Hg ⁰	QF AAS	0.8 ^b	20
Plant, animal	HNO ₃ (bomb)		extrn. by Ni(DDTC) ₂	RNAA	n.g.	103
Mushrooms (0.5 g)	HNO ₃ –H ₂ SO ₄ –H ₂ O ₂	NaBH ₄	volatn. as Hg ⁰	QF AAS	24 ^b	32
Lichens (50–100 mg)	HNO ₃ –HCl (bomb)	SnCl ₂	gold amalgamation	QF AAS	n.g.	111
Wine (5 ml)	HNO ₃ , chromic acid in H ₂ SO ₄	SnCl ₂	volatn. as Hg ⁰	QF AAS	6	19

^a Absolute detection limit, ng; ^b in the sample, ng/g.

(Al₂O₃, MgO, CaO, Florisil) were necessary to ensure complete release of Hg and removal of interfering pyrolysis products [124]. Elimination of interferences from Cu, Pb, Ag, Au, Pt, Pd and Se in reduction of Hg with NaBH₄ by masking with phen and thiosemicarbazide in copper concentrates has been discussed [125].

36.4 SPECIATION

36.4.1 Analytical techniques

The principal interest is in the discrimination among Hg⁰, Hg²⁺, MeHg⁺, Me₂Hg and sometimes Hg-thioneins because of their different behaviour in living organisms and the environment. The two basic types of methods include (1) operational discrimination between inorganic and organic Hg and (2) chromatographic separation of individual species followed by their *on-line* detection.

Non-chromatographic methods

Non-chromatographic methods are based on dividing the total mercury into "inorganic" and "organic" Hg fractions. It is realized either by extraction into a non-polar solvent (the non-extracted fraction is assumed to be inorganic) [97,126,127] or, more often, by selective reduction, usually with SnCl₂ which converts Hg²⁺ to Hg⁰ but does not destroy the C–Hg bonds in R–Hg species [27,49,107,128–132]. After complete purging of the Hg⁰ formed, the same aliquot is treated under oxidizing conditions to break the C–Hg bonds to form Hg(II) which, on its turn, is reduced to Hg⁰. The methods do not distinguish among the particular organomercury species and non-ionic organomercury species which are often included in the inorganic fraction. Operational speciation methods are illustrated in Table 36.4.

Gas chromatographic methods

The small size and volatility allows even ionic methylmercury be chromatographed without derivatization. Reproducibility may be poor owing to uncontrolled adsorption of ionic compounds on the column packing but it can be improved by derivatization with Grignard reagents [83–85]. Hydride generation [108], ethylation with NaBH₄ [5,6, 18,78,92] and iodation with iodoacetic acid [80–82] have also been used for derivatization of the ionic organomercury compounds. Gas chromatographic methods for speciation of organomercury are summarized in Table 36.5.

TABLE 36.4

Operational speciation procedures for speciation analysis for mercury

Sample (amount)	Sample handling	Detection technique	DL	Ref.
Fjord water	volatile: direct; reactive: redn. with SnCl_2 ; total: acidification; redn. with NaBH_4 or $\text{BrCl}/\text{NH}_2\text{OH}\cdot\text{HCl}$; amalgamation with Au	DCP AES	1–2 pg	107
Soft tissues (0.2–0.3 g)	inorganic: digestion with NaOH , cysteine, NaCl ; reduction with SnCl_2 ; total: digestion with NaOH , cysteine, NaCl ; photooxidn., reduction with NaBH_4	FIA CV AAS	inorg. 0.4 $\mu\text{g/g}$; total 0.6 $\mu\text{g/g}$	49
Animal tissues	total: digestion with H_2SO_4 – HNO_3 – V_2O_5 ; redn. with SnCl_2 ; gold amalgamation; total inorg.: digestion with H_2O_2 in NaOH ; redn. with H_2O_2 /gold amalgamation; inorg.: leaching with NaCl in a high ionic strength soln., redn. with SnCl_2 /gold amalgamation	CV AAS	0.6 ng	129
Fish, blood	inorganic: digestion with H_2SO_4 ; redn. with Sn(II) – Cd(II) on ice-bath; org.: digestion with H_2SO_4 ; redn. with alkaline Sn(II) – Cd(II) ; total: digestion with H_2SO_4 – KMnO_4 redn. with SnCl_2	inorg. and org. CV AAS; total: CV DCP AES	4 ng/ml CV AAS; 20 ng/ml CV DCP	130
Foodstuffs, blood	inorganic: conversion into methyl chloride derivative with Me_4Sn extrn. (benzene); back-extrn. into thiosulfate; organic: extrn. into benzene as chloride, stripping into thiosulfate	GF AAS	n.g.	127
BioCRMs	organic: extrn. as chloride into toluene and back-extraction into cysteine acetate	ID ICP MS	5 ng/ml	97

TABLE 36.5

Determination of organic mercury species using GC procedures

Species determined	Derivatization	Column (packing material)	Detection technique	DL (ng/g)	Sample	Ref.
MMHg*	iodide	capillary	ICP AES	0.003 ^a	air	89
MMHg	ICH ₂ COOH	packed (10% AT-100 on Chromosorb W AW)	MIP AES	20	fish, mussels	82
MMHg	ICH ₂ COOH	packed (10% AT-100 on Chromosorb W AW)	MIP AES	1.5	animal tissues	80
MMHg	ICH ₂ COOH	packed (10% AT-100 on Chromosorb W AW)	MIP AES	n.g.	spiked seawater	81
MMHg	NaBEt ₄		CV AFS	0.001 ^a	sediments	92
Hg(II), MMHg, MEHg	BuMgCl	capillary	MIP AES	n.g.	fish, human blood	83, 84
Hg(II), MMHg, MEHg	BuMgCl	capillary	MIP AES	n.g.	tap, natural water	85
Hg(II), MMHg, DMHg	NaBEt ₄	cryotrap (15% OV-3 on Chromosorb W AW-DMCS)	CV AFS	n.g.	fresh, seawater, fish tissue	5
Hg(II), MMHg, DMHg	NaBEt ₄	packed (10% OV-3 on Chromosorb W AW-DMCS)	QF AAS	n.g.	fish tissue	7
Hg(II), MMHg, DMHg	NaBEt ₄			n.g.	biological materials	8

continued

TABLE 36.5 (continuation)

Species determined	Derivatization	Column (packing material)	Detection technique	DL (ng/g)	Sample	Ref.
Hg(II), MMHg, DMHg, DEHg	none	packed (15% OV-3 on Chromosorb WAW-DMSC)	CV AFS	0.002 ^a	air	90
DMHg, DEHg, MEHg, MMHg	none	packed (I: 2% BOSP on Chromosorb W AW DMSC, II: 15% DEGS on Shimalite AW)	QF AAS	0.2 –0.5 ^a	air	110
MMHg, MEHg, DEHg, MPhHg	none	capillary	CV AAS	40	fish	133
MMHg	NaBEt ₄	packed (15% OV-3 on Chromosorb WAW-DWSC)	CV AFS	0.0001 ^a	rain, lake water, snow	18
MMHg	none	packed (5% DEGS on Supelcoport)	DCP AES	0.3 ^a	fish	134

^a Absolute detection limit, ng.

*MMHg = MeHg⁺; MEHg = MeEtHg; DMHg = Me₂Hg; DEHg = Et₂Hg; MPhHg = MePhHg.

Liquid chromatographic methods

Mercury species can be separated comprehensively by reversed-phase LC on their complexation in the mobile phase by 2-mercaptoethanol [135–139] or cysteine [140], or on a prior chelation with dithizone [141]. Cation-exchange chromatography [142] and electrophoresis [143] were proposed for the separation of cationic mercury species. Mercury-containing thioneins have been separated by SEC [144]. Post-column reduction [138,140,142,145] is often used to improve the transport of the analytes to the detector. Applications of LC to mercury speciation are summarized in Table 36.6.

TABLE 36.6

Liquid chromatographic separations for Hg speciation analysis

Analyte	Separation (column)	Mobile phase	Detection	Sample	Ref.
Hg(II), MMHg*, MEHg, MPhHg	ion-interaction chromatogr.(C18)	5 mM APS, 20% acetonitrile	ICP MS	urine	146
MMHg, benzoyl- mercury	reversed-phase chromatogr. (Chromospher RP18)	0.1 mM 2- mercaptoethanol, CH ₃ COONH ₄ , pH 5, gradient 30–50% MeOH	UV	soil extracts	117
Hg(II), MMHg, MEHg	reversed-phase chromatogr. (Chromospher RP18)	0.1 mM 2- mercaptoethanol, CH ₃ COONH ₄ , pH 5, gradient 30–50% MeOH	CV AFS	sediments	138
Hg(II), MMHg, MEHg, MPhHg	normal-phase chromatogr. (ODS)	0.05 M acetate buffer, pH 4, 0.05 mM EDTA, THF- MeOH (2:1)	VIS	urine, tap water, potatoes	141
Hg(II), MMHg, MEHg, thimerosal	reversed-phase chromatogr. (Waters PicoTg C18)	0.06 M CH ₃ COONH ₄ , 3% acetonitrile, 0.005% 2- mercaptoethanol, pH 5.3–6.8	ICP MS	tuna, contact lens solution	136
MMHg, DMHg	reversed-phase chromatogr. (C18 Hypersil ODS)	1.5 M HCl, acetonitrile	CV AAS	standards	127
Hg(II), MMHg	reversed-phase chromatogr. (Bischoff ODS-II)	0.1 M CH ₃ COOH, 40 mM cysteine	CV AAS	dolphin liver	147
Hg(II), DMHg, DEHg, DPhHg	reversed-phase chromatogr. (C18)	10 mM CH ₃ COOH– MeOH (80:20), pH 6.2, 0.1 M 2- mercaptothiazole	UV	standards	148

continued

TABLE 36.6 (continuation)

Analyte	Separation (column)	Mobile phase	Detection	Sample	Ref.
Hg(II), MMHg, MEHg, thimerosal	reversed-phase chromatogr. (Vydac 201 TP C18)	0.06 M CH ₃ COONH ₄ , 0.1% 2- mercaptoethanol, 1.5% acetonitrile, 3% MeOH	ICP MS	wastewater, contact lens soln., DORM-1	139
MMHg	reversed-phase chromatogr. (Zorbax ODS)	MeOH- CH ₃ COONH ₄ , pH 5.7	CV AAS	seafood	132
Hg(II), MMHg, MEHg, DMHg	reversed-phase chromatogr. (C18)	0.06 M CH ₃ COONH ₄ , 0.005% 2-mercap- toethanol	ICP AES	spiked water	135
Hg(II), MMHg	reversed-phase chromatogr. (STR ODS H)	0.04 M cysteine, 0.1 M CH ₃ COOH	CV AAS	wastewater	140
Hg(II), MMHg, MEHg	cation exchange (Dionex CG-5)	1 mM CH ₃ COOH, CV AAS 1 mM NaClO ₄ , 5 mM cysteine, pH 4.4	CV AAS	tap water	142
Hg-thioneins	size-exclusion (Asahipak GFA- 30F)	0.2 M (NH ₄) ₂ SO ₄ , ICP MS 0.05 M Tris, 1 mM EDTA buffer, pH 7.5	ICP MS	cyano- bacterium	149, 150
Hg-thioneins	size-exclusion (TSK G 2000 SW)	0.03% NaN ₃ , UV 10 mM Tris-HCl buffer, 100 mM NaCl, pH 7.0	UV	mussels	144
Hg(II), MMHg, MEHg, MPhHg	capillary zone electrophoresis	cysteine, borate buffer pH 8.35, sodium dodecylsulfate	UV	mussels	143

*See p. 532

36.4.2 Speciation analysis of real samples

Water

Storage conditions to preserve Hg species in rain water have been discussed in terms of the total, ionic and organic mercury recovery [115] with emphasis on methylmercury [114]. Methylmercury decomposes rapidly in the absence of any additions of other reagents, the best preservative is 5% NaCl followed by 1% HNO_3 or HCl whereas the best container material is glass [114]. Bacterial contamination which not only breaks methylmercury down to inorganic mercury but also reduces Hg^{2+} to volatile Hg^0 should be avoided. Electrochemical separation of Hg^{2+} and MeHg^+ by electrodeposition of Hg^{2+} on a Pt electrode at -1.0 V has been reported whereas for MeHg^+ -0.2 V or even more negative potentials were required [131]. Volatile mercury was purged directly and inorganic mercury was reduced with SnCl_2 , whereas the total was determined after reduction with NaBH_4 or $\text{BrCl}/\text{NH}_2\text{OH}$ in fjord water [107]. Selective reduction is achieved with SnCl_2 for inorganic Hg and SnCl_2 – CdCl_2 for total Hg. Prior to GC, Hg species are usually derivatized *in situ* by ethylation with NaEt_4 [5,18], trapped on a GC sorbent and selectively released to the detector. Extraction of Hg species as DDTC complexes into benzene followed by their butylation is an alternative [85]. Use of LC methods is limited to waste waters [140] because of the inadequate sensitivity for natural waters. Speciation of Hg in natural waters has been discussed [151].

Sediments

Differential determination of organomercury, HgO and HgS in marine sediments has been based on the extraction of organic Hg into CHCl_3 , back-extraction into a 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution and leaching of HgO and HgS with H_2SO_4 and HCl – CuCl , respectively [152]. Distillation was recommended for the isolation of methylmercury from sediment samples, its main advantage over alkaline digestion is the avoidance of matrix effects during subsequent ethylation (for GC–CV AFS determination) [92]. HCl leaching was found ineffective in quantitatively releasing MeHg from sediments and for concentration higher than 4 M HCl decomposition of MeHg was observed [92]. Determination of methylmercury in a CRM Marine Sediment CRM has been discussed [153].

Biomaterials

The effects of long-term storage of wet samples in a deep-freeze, thermal cycling, freeze drying and γ -irradiation on the stability of

methylmercury in fish, shellfish, human hair, blood and appropriate CRMs have been investigated [154]. Fresh and dried fish show good stability with time and against temperature cycling. Shellfish and blood should not be repeatedly frozen and thawed; otherwise possible losses of methylmercury can occur. Losses of methylmercury of up to 30% from wet mussels occurred on prolonged storage in a deep-freeze. Gamma-irradiation reduced the methylmercury content for some fish and shellfish species [154]. Sample pretreatment should separate free Hg(II) without breaking C-Hg bonds. The classical Westöö method involves benzene (toluene) extraction from acidified fish tissue homogenate, back-extraction into cysteine acetate and a final extraction of the alkylmercury salt from the cysteine solution with benzene [97,155]. Methylmercury has been isolated from seafood by extraction with CHCl_3 , elution from a diatomaceous earth column with HCl and extraction of organomercury with thiosulphate [156]. Digestion with a strong alkali such as NaOH, KOH or Me_4NOH was proposed. Cysteine is recommended to liberate inorganic mercury from organic matrix and to protect the C-Hg bond. Different isolation techniques (ion exchange, extraction, volatilization, distillation) and measurement by CV AAS or GC ECD have been compared for methylmercury determination [16]. Selective leaching of organomercury compounds from human hair has been discussed [157]. In the improved procedure H_2SO_4 was used to release methylmercury from a biological matrix [80]. In chromatographic methods the organic mercury in the solution obtained after mild digestion is purged as iodide [80–82], hydride [158] or ethylate [5,7,8]. Alternatively methylmercury can be extracted into toluene and butylated with a Grignard reagent [83,84].

Interlaboratory surveys for methylmercury in animal blood and brain tissues [159], seafood by HPLC–CV AAS [156], biological tissues [160], fish and mussels [161] have been reported. Several CRMs with certified content of methylmercury are available (e.g. NRCC DORM-1 dogfish muscle). An intermethod survey for methylmercury in environmental and biological materials has been carried out [162].

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Molybdenum

Molybdenum (Mo, atomic weight 95.94, melting point 2617°C , $d = 10.22\text{ g cm}^{-3}$) is a silver white hard metal. It occurs in the earth's crust with an average abundance of 1.5 ppm, primarily as molybdenite (MoS_2). The metal dissolves in HNO_3 , *aqua regia* and concentrated $\text{HCl-H}_2\text{SO}_4$, and is attacked by fused alkali-metal hydroxides. All oxidation states from II to VI of Mo are known, Mo(VI) being the most stable. In strongly acidic solution, Mo(VI) exists as the green molybdenyl ion, MoO_2^{2+} , whereas in alkaline solution the molybdate, MoO_4^{2-} , is present. In the intermediate pH range isopolyanions exist. Molybdenum is an amphoteric element with predominantly acidic properties. Molybdenum(VI) has no strong oxidizing properties. Depending on the reducing agent used and on the reduction conditions, Mo(VI) is reduced to a mixture of lower oxidation states. Molybdenum(VI) forms heteropolyacids (e.g. with Si, P, V(V), As(V) and Ge) and fluoride, chloride, peroxide, citrate and oxalate complexes. Molybdenum is a biologically essential element and a component of many enzymes [1,2]. It is widely applied as an additive to steels, in catalysts and as a substrate in the production of ^{99}Tc . The analytical chemistry of Mo has been the subject of a monograph [3].

37.1 SEPARATION AND PRECONCENTRATION

Extraction

Molybdenum is extracted as the chloride complex from 6–7 M HCl media into *O*-donor solvents; co-extraction of Fe(III) is prevented by its reduction with iodide [4]. Extraction of the Mo- α -benzoinoximate from acid medium (0.01–2 M HCl) into CHCl_3 is a fairly selective method for the separation of Mo (W, V, Cr and Pd are co-extracted unless masked

or reduced) [5,6]. Various chelating extraction systems including dithiol (MIBK) [7] benzohydroxamic acid (hexanol) [8], BPHA (CHCl_3 , toluene) [9–11], di(2-ethylhexyl)phosphoric acid (cyclohexane) [11,12], 5,5'-methylenedisalicylohydroxamic acid (MIBK) [13], 8-hydroxyquinoline (DIBK, CHCl_3) [14,15], DDTC (CHCl_3) [16] and TOPO (MIBK) [17] have been reported for the separation of Mo(VI), usually from strongly acidic media. A comparison study of several extractants has been presented [11]. To improve selectivity Mo can be masked with H_2O_2 while the interferents are extracted, then demasked (e.g. by boiling with HCl or KMnO_4) and finally extracted itself [16]. The common Fe(III) interference is usually removed by its reduction with ascorbic acid (Mo(VI) is reduced to Mo(V)) [16].

Sorption

Strong anion exchangers retain Mo(VI) as the chloride [18,19], citrate [20] or azide [21] complex. Alternatives include sorption of Mo(VI) on activated alumina (pH 2–4) [22] or chelating resins [23,24], or sorption of Mo chelates on activated charcoal [25–27]. Quantitative elution of Mo is often problematic; a broadly tailing elution pattern is encountered [18,19].

Other methods

Molybdenum precipitates from acid media as MoS_3 with Cu or Sb as collectors or as hydroxide (at pH 4), e.g. on Fe(III)-loaded cellulose [28]. Molybdenum can be volatilized as carbonyl Mo(CO)_6 [29] or fluoride [30].

37.2 DETERMINATION TECHNIQUES

Spectrophotometry

In the presence of reducing agents (e.g. ascorbic acid, SnCl_2) Mo(VI) reacts in acid media with thiocyanate to give an orange–red extractable complex ($\epsilon \sim 1.6 \times 10^4$ at 470 nm). Another method is based on the reaction of dithiol with Mo(VI) in strongly acidic media (4–12 M HCl , 3–7 M H_2SO_4) to form a green complex extractable with various organic solvents ($\epsilon = 2.1 \times 10^4$ at 675 nm). Iron(III) must be reduced whereas W is masked with citrate or tartrate. Higher sensitivity ($\epsilon = 2.1 \times 10^5$) is obtained, e.g. by ion pairing of the Mo anionic complex with 3,5-dinitro-catechol with Rhodamine B [31]. The catalytic effect of Mo on the

oxidation of iodide by H_2O_2 in acidic medium is the basis of a sensitive but poorly selective method [5,6,32]. Generally, spectrophotometric methods should not be used except after selective separation of Mo from the matrix. Spectrofluorometric determination of Mo is based on its reaction with Alizarine Red S [33,34].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.7 \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame at the most sensitive 313.3 nm line [10,35]. The Mo signal is depressed by the presence of Ca, Sr, Fe and sulphate. The interferences can be controlled by the addition of AlCl_3 , NH_4Cl or Na_2SO_4 . Increasing the sensitivity by aspirating the MIBK solution is hampered by the fact that organic ligands may enrich the flame with oxidizing entities which preclude complete atomization of Mo in the flame [13,36]. Conversion of the chelates into the thiocyanate complex (remaining in the organic phase) has been proposed as a remedy [13].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of 0.02 ng ml^{-1} (characteristic mass 9 pg). Owing to the refractory nature of Mo, high ashing temperatures may be used without loss of the element [38]. Mechanisms of atomization of Mo in the graphite furnace have been comprehensively discussed [39,40]. The technique suffers from carbide formation, sensitivity drifts and memory effects. Uncoated and pyrocoated graphite, metal (La, Zr) carbide and tantalum atomization surfaces were examined [41]. The graphite of uncoated tubes can easily interact with Mo to produce non-volatile (melting point $\sim 2700^\circ\text{C}$) carbides (Mo_2C and MoC) which reduce atomization efficiency and sensitivity, and may also result in carry-over [37]. Use of pyrolytically coated tubes minimizes formation of the carbides [38] and allows for a high heating rate required for the atomization step by using volatilization from the tube wall [37]. Carbide formation was also reduced by injection of the sample into a pre-heated furnace (100°C) [38] or by use of a thermally shielded furnace [42]. The carbide formation is enhanced by the carbon deposits from undigested samples [15,43–45] and results in tailed atomization peaks. Changes in peak shape and sensitivity drift associated with the corrosion of the pyrolytic graphite layer by acid and the high atomization temperatures used can be circumvented by the measurement of peak area (instead of peak height) and frequent recalibration [46–49].

The variable quality of commercial tubes often leads to contradictory results reported [37,47]. In the presence of K, Ca, Mg, Na and P the molybdenum absorption signal increases progressively with increasing number of firings and peaks become narrower, but no significant change in peak area is observed [49]. Memory effects are common. They can be identified by the release of some Mo species tightly chemisorbed on the graphite tube when an acidified solution is injected as a blank [40]. A high temperature (*ca* 3000°C) clean-out is usually necessary but the tube lifetime is thus shortened [15,43–45]. Memory effects can be decreased by some acids (e.g. HCl and salts, especially BaF₂ [44,45]) which facilitate formation of more easily atomizable Mo species [40].

Sulphate [27,50], phosphate [27] and HNO₃ [46] were found to depress the Mo signal. The SO₄²⁻ interference was removed by CaCl₂ and Ni(NO₃)₂ but the latter had the disadvantage of producing a negative blank absorbance and contributing to tube fouling [50]. The important elemental interferences were due to Al, Fe, Ca, Mg, W and V [37,43,46]. Interference with La, Ce, Mg, Ca, Sr and Ba can be reduced by H₃BO₃ [36]. Various matrix modifiers including BaF₂ [43–45,51], Mg(NO₃)₂ [45], ascorbic acid [52,53] and Pd–NH₂OH [54] have been proposed. The most efficient seems to be BaF₂ which decreases the appearance temperature of Mo, increases the signal and overcomes matrix interference effects owing to the preferential formation of volatile Mo fluoride. Analysis of real samples requires background correction, either D₂ [37,43–46,52,53] or Zeeman effect [51,54,55].

Atomic emission spectrometry

The molecular emission of molybdenum oxide was found to be analytically useful in H₂-based flames; however, there were poor DLs [56]. The ICP AES recommended wavelength is 202.030 nm (DL 8 ng ml⁻¹); other lines include 281.615 nm, 287.151 and 277.540 nm with DLs of 15–30 ng ml⁻¹ [22]. Electrothermal vaporization ICP AES offers a DL of 0.7 ng ml⁻¹ [30]. Calcium, Mg and Al are the most serious interferents [46]. Molybdenum is introduced into the plasma after separation from the matrix by coprecipitation [57] or sorption [22,25,26,58]. General problems related to the introduction of organic Mo extracts into plasma have been discussed [4]. Extracts of the Mo–chloride complex in heptan-2-one and of the Mo–dithiol complex in *i*-PrOH could be fed into the ICP [4] and DCP [7], respectively. Because of the large background noise at 202.030 nm, the 281.615 nm line was used for the DCP AES measurements [7]. The volatility of Mo can be enhanced by fluorination [30],

carbonyl formation [29] or *S*-containing thermochemical agents, e.g. DDTC or xanthate [59].

Mass spectrometry

Molybdenum has seven stable isotopes: ^{92}Mo (14.8%), ^{94}Mo (9.35%), ^{95}Mo (15.9%), ^{96}Mo (16.7%), ^{97}Mo (9.6%), ^{98}Mo (24.1%) and ^{100}Mo (9.6%). Many isotopic overlaps include natural ^{96}Ru , ^{98}Ru and ^{100}Ru and ^{92}Zr , ^{94}Zr and ^{96}Zr [12], potassium ions (^{94}Mo : $^{39}\text{K}^{39}\text{K}^{16}\text{O}$, ^{95}Mo : $^{40}\text{Ar}^{39}\text{K}^{16}\text{O}$, ^{96}Mo : $^{39}\text{K}^{41}\text{K}^{16}\text{O}$ and ^{97}Mo : $^{40}\text{Ar}^{41}\text{K}^{16}\text{O}$), bromine $^{79}\text{Br}^{16}\text{O}^+$ at $m/z = 95$ and $^{81}\text{Br}^{16}\text{O}^+$ at $m/z = 97$ [60–63], $^{84}\text{SrO}^+$ and NaKCl^+ coincident with $^{100}\text{Mo}^+$ [63] which should be carefully evaluated. Thermal ionization can be enhanced by adding H_3BO_4 [19]. Isotopic ratios were corrected for mass fractionation by iterative normalization using the 96:98 count ratio [19]. ICP MS offers a DL of 10 pg ml^{-1} . The most abundant ^{98}Mo is usually selected for quantification [60,62,64]. In IDA ^{95}Mo [64] or ^{97}Mo [28] is used as a spike.

Neutron activation analysis

Neutron activation analysis is based on the reaction $^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$. The ^{99}Mo ($t_{1/2} = 66.2 \text{ h}$) decays through β -emission to a radioactive daughter $^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6.0 \text{ h}$, $E_\gamma = 140.5 \text{ keV}$) which is counted [16,65]. The measurements should be carried out at least 30 h after irradiation when equilibrium between ^{99}Mo and $^{99\text{m}}\text{Tc}$ is established and both activities decay with the parent's half-life. The strong Compton continuum of ^{24}Na and ^{42}K γ -rays and *bremssstrahlung* due to high energy β -radiation of ^{32}P render it difficult to count the $^{99\text{m}}\text{Tc}$ activity. Spectral interferences of the 142.5 keV ^{59}Fe photopeak may create a problem at the Fe:Mo ratios higher than 1000 [65].

37.3 ANALYSIS OF REAL SAMPLES

Natural waters

Natural waters contain *ca* 10 ng ml^{-1} Mo. They can be analyzed directly by GF AAS using D_2 or Zeeman background correction and matrix modifiers with DLs of $1\text{--}4 \text{ ng ml}^{-1}$ [50,52,54]. Uncoated tubes are preferred for the NaCl matrix because an ashing temperature exceeding the boiling point of NaCl can be used without loss of Mo [41]. Ten-fold dilution and correction of both spectral and non-spectral interferences were shown to be sufficient to allow accurate determination of

TABLE 37.1

Determination of molybdenum in water samples

Water (amount)	Separation/ preconcentration	Detection	DL (ng/ml)	Ref.
CRM	<i>on-line</i> sorption on activated alumina	ICP AES	0.2	22
Sea, lake (0.1–0.2 l)	anion exchange of azide complex, elution with NH_4Cl – $\text{NH}_3(\text{aq})$	GF AAS		21
River (0.2 l)	UV photolysis, copptn. with Fe(III)- loaded cellulose	GF AAS ICP AES	0.05	57
River (0.1 l)	sorption on activated charcoal	ICP AES	0.4	26
River (0.1 l)	sorption on activated charcoal	ICP MS	0.06	26
Mineral (1 l)	anion exchange as $\text{Mo}(\text{SCN})_4^-$, elution with 2 M HClO_4 /1 M HCl	ICP AES	0.01	58
Mineral (1 l)	anion exchange, elution with HClO_4 – HCl	GF AAS	0.05	20

Mo in seawater CRMs by ICP MS [63]. Macromolecular complexes in natural water have been separated by SEC and detected by GF AAS or ICP AES [66]. Analytical procedures are summarized in Table 37.1.

Geological materials

Soil leachates [37,46] and ore digests [53] can be analyzed directly by GF AAS with D_2 background correction and Pd [37], $\text{Mg}(\text{NO}_3)_2$ [46] or ascorbic acid [53] matrix modifiers to give ADLs of 8–80 pg. An alternative is ICP MS employed after a separation–preconcentration step [64] or after alkaline fusion and ETV (DL $0.03 \mu\text{g g}^{-1}$) [67]. Combined analytical procedures are summarized in Table 37.2. Speciation in soils is based on the differentiation between the mobile fraction (extraction with ammonium acetate (pH 7.0) [38] or with ammonium oxalate–oxalic acid mixture (pH 3.3) [42]) and the total Mo content (*aqua regia* attack).

Clinical samples

The analysis of clinical samples for Mo has been reviewed [68]. Stainless steel equipment must not be used for sampling; class-100 environment was recommended for sample handling [8]. Typical blanks

TABLE 37.2

Determination of molybdenum in geological samples

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
CRM rocks, sediments (0.2 g)	fusion with $\text{Na}_2\text{CO}_3\text{--NaNO}_3$, leaching with H_2O	sorption of the 8- hydroxyquinoline complex on charcoal	ICP AES	0.2	25
CRM Cu-ores, concentrates (0.5 g)	HF--HClO_4 or fusion with $\text{K}_2\text{S}_2\text{O}_7$	extrn. with BPHA (toluene)	FAAS	n.g.	10
CRM rocks (0.1–1 g)	HNO_3 , HF (microwave assisted)	extrn. with BPHA (CHCl_3)	ICP MS	0.1 ^a	9
CRM rocks (0.1 g)	fusion with LiBO_2 , dissoln. in HCl	sorption of the complex with dithiophosphoric acid O, O-diethyl ester on charcoal, desorption with HNO_3	FAAS GF AAS	n.g.	27
CRM soil, sludge, sediment (2–5 g)	<i>aqua regia</i>	none	GF AAS	n.g.	38
CRM rock, soil, sediment (0.20 g)	fusion with $\text{Na}_2\text{CO}_3\text{--NaNO}_3$, leaching with H_2O	sorption of the complex with 8-hy- droxyquinoline on charcoal, ashing	ID ICP MS	0.08	64
Rocks, soils, sediments (0.25 g)	HCl	extrn. of the chloride complex (heptan-2-one)	ICP AES	0.06	4
Meteorites (2–5 g)	HCl (microwave assisted)	extrn. with di(2- ethylhexyl)phos- phoric acid (cyclohexane), back-extrn. with $\text{HNO}_3\text{--H}_2\text{O}_2$	TI MS	n.g.	12

continued

TABLE 37.2 (continuation)

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Soil (2 g)	leaching with <i>aqua regia</i>	none	GF AAS	75 ^b	37
Soil (15 g)	leaching with H_2O	none	VIS	1.3 ^a	32
Soils, sediments (1 g)	fusion with LiBO_2 , dissoln. in HCl	extrn. with TOPO (MIBK)	FAAS	0.5	17
Soils (12.5 g)	leaching with $\text{CH}_3\text{COONH}_4$	none	GF AAS	8 ^b	46
Soil (1 g)	digestion with HClO_4 -HF, HCl	extrn. with 5,5'- methylenedisalicylo- hydroxamic acid (MIBK), conversion into Mo-SCN complex	FAAS	30 ^a	13

^a In the solution fed, ng/ml; ^b absolute detection limit, pg.

for quartz ampoules used in NAA are about 1 ng and exceed the normal serum level. Flame AAS is not sufficiently sensitive for biomedical samples. Undigested serum [45] or human milk [43,44] can be analyzed directly by GF AAS with BaF_2 matrix modifier and D_2 background correction with a DL of 1 ng ml^{-1} , which is often insufficient. The carbon deposits from undigested samples enhance the formation of refractory Mo carbides in the direct analysis of milk [43,44] and serum [45]. Digestion is necessary as matrix modifiers may not otherwise be adequate to eliminate matrix effects [45,51]. The ICP MS DL (taking into account a 5-fold dilution) was 0.44 ng g^{-1} in lyophilized serum [60-62]. Thermal ionization MS has been applied to the determination of isotope ratios in urine and faeces for stable isotope studies of the Mo metabolism [19].

Non-clinical biomaterials

Owing to the refractory nature of Mo, dry ashing is an accepted procedure for the destruction of organic matter and has been recom-

mended for all types of foodstuffs except fatty fish [69]. The mixture of $\text{HNO}_3\text{--H}_2\text{SO}_4$ gave good results but caused the graphite tube in GF AAS determination to deteriorate; $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--HClO}_4$ digestion resulted in poor reproducibility and low recovery for all meats, eggs, bread and flour [65]. Extraction with dilute HCl was adequate for meats, white fish, flour and vegetables, but failed for eggs, milk, fruit, potatoes and fatty fish [69]. Food digests can be analyzed directly by GF AAS with D_2 background correction with a DL of $0.5\text{--}0.8\text{ ng ml}^{-1}$ [69]. Direct GF AAS has been successfully applied to the analysis of plant samples after $\text{HNO}_3\text{--H}_2\text{O}_2$ digestion [48] or dry ashing [42]; H_2SO_4 was found to depress the GF AAS signal [48]. Owing to the low Mo contents in plants it was not possible to determine it by FAAS (even after extraction preconcentration); GF AAS was recommended [7]. Analytical procedures for the determination of Mo in biological materials are summarized in Table 37.3.

Industrial samples

Molybdenum is usually included in the multielement array during trace element characterization of various materials, especially steels (seldom at the trace level) and wear oils (MoS_2 is applied as an additive for motor oils). Procedures relevant to trace analysis can be found in the tables in Chapters 11 and 12.

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TABLE 37.3

Determination of molybdenum in biological materials

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL	Ref.
Serum, plasma (1 ml)	HNO ₃ -H ₂ SO ₄ -HClO ₄	extrn. with 8-hydroxyquinoline (CHCl ₃)	GF AAS		15
Serum (2 ml)	HNO ₃	extrn. with benzo-hydroxamic acid (hexanol)	GF AAS	0.1 ^a	8
Faeces	dry ashing, dissoln. in HCl	anion exchange, elution with 1 M HCl	TI MS		19
Plants (2-4 g)	HNO ₃ -H ₂ SO ₄ -HClO ₄	extrn. with dithiol (MIBK)	GF AAS		7
Plants (2-4 g)	HNO ₃ -H ₂ SO ₄ -HClO ₄	extrn. with dithiol (<i>i</i> -AmOH)	DCP AES	0.5 ^a	7
Plants (1 g)	dry ashing, dissoln. in HCl	extrn. with α-benzoin-oxime (CHCl ₃)	VIS		6
Plants (1-4 g), soils (0.2-0.3 g), CRMs	dry ashing, fusion with NaOH	extrn. with Zn(DDTC) ₂ (CHCl ₃) back-extrn. (H ₂ O ₂)	RNAA	1 ^b	16
Plants, CRMs	dry ashing	extrn. with α-benzoin-oxime (CHCl ₃)	VIS	5 ^a	31
CRMs	dry ashing, dissoln. in HCl	sorption of the Mo-complex with dithiophosphoric acid <i>O,O</i> -diethyl ester on activated carbon, elution with HNO ₃	GF AAS		27
CRMs (1.0 g)	dry ashing, dissoln. in HNO ₃		ID ICP MS		28

^a ng/ml in solution fed; ^b absolute detection limit, ng.

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Nickel

Nickel (Ni, atomic weight 58.71, melting point 1453°C, $d = 8.9 \text{ g cm}^{-3}$) is a silver-white, hard, malleable, ductile, ferromagnetic metal. It occurs in the earth's crust with an average abundance of 0.008%, primarily in sulfide ores. Crude oils contain significant amounts of Ni porphyrines. The metal is passivated by cold concentrated HNO_3 but it dissolves readily in dilute HNO_3 , in hot concentrated HNO_3 and in *aqua regia*. It is readily attacked by HCl but only in the presence of a catalyst, e.g. Pt(IV) . Alkalis in solution or in the molten state do not affect Ni. In aqueous solution Ni exists only in the II oxidation state as the green Ni^{2+} ion. Nickel hydroxide precipitated at $\text{pH} \sim 7$ is insoluble in alkalis but dissolves in $\text{NH}_3(\text{aq})$. Nickel forms stable ammino, cyanide, tartrate, citrate and EDTA complexes. Nickel is a common constituent of steels and an important catalyst and is used in many industries (electroplating, batteries etc.). Nickel is an allergenic and some of its compounds are carcinogenic. The demand for its trace analysis is particularly acute in clinical toxicology and occupational hygiene.

38.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of the Ni complexes with dimethylglyoxime (H_2Dm) or other dioximes into CHCl_3 is the most popular, especially when followed by spectrophotometric determination. Alternatively, Ni can be extracted as a complex with dithiocarbamates [1–5] or with 1,5-bis(di-2-pyridylmethylene)thiohydrazide and its derivatives [6–9].

Volatilization

Volatilization of Ni as $\text{Ni}(\text{CO})_4$ is widely employed [10–13]. Nickel (II) is reduced by NaBH_4 to Ni^0 that, in its turn, reacts with CO to give $\text{Ni}(\text{CO})_4$. The latter is then stripped from the reactor by a carrier gas. Metallic iron hampers the formation of $\text{Ni}(\text{CO})_4$ but this interference is avoided by carrying out the reaction in 2% HNO_3 in which Fe(III) is reduced to Fe(II) without the formation of Fe^0 [10]. The generation of $\text{Ni}(\text{CO})_4$ is fast enough to be carried out *on line* [11]. The carbonyl formed can be preconcentrated cryogenically [12] or by trapping in a graphite furnace [13]. The Ni complex with *bis*(trifluoroethyl)dithiocarbamate is sufficiently volatile to be separated by GC [4].

Ion exchange and sorption

Nickel is retained by anion exchangers from 9 M HCl [14,15] and by chelating resins containing imminodiacetic [16,17] or carboxymethyl groups [18]. Sorption of Ni on dioxime-loaded naphthalene [19] or as a dithiocarbamate complex on inert resins [20] is an alternative.

Coprecipitation

Coprecipitation of the Ni dimethylglyoximate with Pd as collector is almost specific. Alternatively Ni can be precipitated with APDC [21]. Precipitation of $\text{Ni}(\text{OH})_2$ on CaCO_3 or MgCO_3 has been reported [16]. *On-line* precipitation with 1-nitroso-2-naphthol has been developed [22].

38.2 DETERMINATION TECHNIQUES

Spectrophotometry

Dimethylglyoxime reacts with Ni^{2+} in a neutral or an NH_3aq medium to form a pink chelate extractable into CHCl_3 which forms the basis of a poorly sensitive ($\epsilon = 3.4 \times 10^3$ at 260 nm and 1.8×10^3 at 400 nm) but highly selective method. In an alkaline medium in the presence of oxidants (e.g. Br_2 or $\text{S}_2\text{O}_8^{2-}$) an intensely coloured ($\epsilon = 1.5 \times 10^4$ at 445 nm) water-soluble $\text{Ni}(\text{Dm})_3^{2-}$ complex is formed. To avoid the interference of colour ions the latter method is preceded by extraction of Ni. Methods using PAR ($\epsilon = 7.5 \times 10^4$ at 493 nm) [16] or 5-Br-PADAP ($\epsilon = 1.26 \times 10^5$ at 560 nm) are more sensitive but lack the selectivity.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.1\text{--}0.2 \mu\text{g ml}^{-1}$ at the most sensitive 232.0 and the 231.1 nm lines in the recommended air- C_2H_2 (oxidizing,

lean, blue) flame [19]. The sensitivity is considerably increased by sample introduction as $\text{Ni}(\text{CO})_4$, especially after a cryopreconcentration or by using a QF atom trap. Hydride-forming elements are potential interferents in this method; because of the Sn interference it was necessary to choose the 341.5 nm line at the expense of sensitivity [10]. With multielement lamps containing iron, interference may occur when the 232.0 nm line is used.

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 10 pg (DL of 0.1 ng ml^{-1}). Nickel has a high atomization temperature (2700–3000°C) and can be separated by selective volatilization of the matrix in the graphite furnace [23]. Matrix modification is generally unnecessary but HNO_3 is usually added. Pyrocoated tubes are recommended to avoid carbide formation [23–31]. High nonspecific absorption occurs close to the 232.0 nm line, necessitating the removal of NaCl [23]. Addition of H_2 to the Ar purge gas improved the peak shape, peak height and reproducibility, reduced the noise and resulted in a prolonged tube lifetime [32]. A special design for the analysis of large amounts of solid samples has been proposed [33].

Atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 5–10 ng ml^{-1} at the most sensitive 221.65, 231.60 and 216.56 nm lines. The 221.65 nm line is interfered with by Si, the 231.6 nm line by Co and the 216.56 nm line by Fe. The use of the alternative 352.454 nm line has been reported [6–8]. Introduction of $\text{Ni}(\text{CO})_4$ into the MIP drew considerable attention [12,20]. An ADL of 0.1 ng was reported for ETV MIP AES [34].

Neutron activation analysis

Reactor irradiation of Ni by thermal neutrons leads to long-lived ^{63}Ni ($t_{1/2} = 125 \text{ y}$, β -emitter) and short-lived ^{65}Ni ($t_{1/2} = 2.56 \text{ h}$, β - γ -emitter, $E_\gamma = 0.37, 11.12, \text{ and } 1.5 \text{ MeV}$). The latter is usually used. A chemical separation is often involved to avoid spectral interference from other short lived nuclides. An alternative is the fast neutron induced reaction $^{58}\text{Ni}(\text{n,p})^{58}\text{Co}$ ($t_{1/2} = 71 \text{ d}$) [13,15]. In contrast to ^{64}Ni , ^{58}Ni has high isotopic abundance and the γ -counting characteristics of ^{58}Co are advantageous [15].

Mass spectrometry

Nickel has five stable isotopes, ^{58}Ni (68.27%), ^{60}Ni (26.10%), ^{61}Ni (1.13%), ^{62}Ni (3.59%) and ^{64}Ni (0.91%), and is readily amenable to TI

MS. Determination of Ni by ICP MS is hampered by the overlap of Ca oxides and hydroxides, $^{42}\text{Ca}^{16}\text{O}^+$, $^{40}\text{Ca}^{18}\text{O}^+$ and $^{44}\text{Ca}^{16}\text{O}^+$, and some NaK ions with each of the major Ni isotopes [35,36]. The interferences were eliminated mathematically, enabling the determination of Ni with a DL of 1 ng ml^{-1} [35], by cryogenic desolvation [36,37] or by the separation of Ni from the interfering ions [20]. Addition of a small dose (2%) of H_2 to the aerosol gas flow enhanced analyte signals by a factor of 2–3, which compensated for the loss of analyte signal that accompanied earlier efforts at cryogenic desolvation [36]. Volatile Ni compounds, e.g. the bis(trifluoroethyl)dithiocarbamate complex are amenable to GC ID MS after spiking with ^{62}Ni [4].

Fluorescence techniques

Wavelength dispersive XRF offers a DL of $0.08\text{ }\mu\text{g g}^{-1}$ in fuel and residual oils [38]. Non-resonance LE AFS in an air- C_2H_2 flame offered a DL of 0.5 ng ml^{-1} [39]; with ETV an ADL of 10 fg was reported [40].

38.3 ANALYSIS OF REAL SAMPLES

The Ni levels in ores are readily accessible by FAAS whereas in other geological and industrial materials Ni is often determined in a multielement array (see Part II). The Ni concentrations in environmental, biological and especially clinical materials are low and require customized approaches [41]. Speciation of Ni is enjoying increasing interest, especially regarding porphyrin complexes. Significant heterogeneity of airborne nickel speciation has been found; soluble salts (Ni^{2+}), metallic Ni^0 and insoluble oxides (NiO_x) were identified in dust and air particulates [42].

Water

In natural waters the dissolved forms can include the hydrated Ni^{2+} cation, complexes with inorganic ligands (e.g., CO_3^{2-} , OH^- , Cl^-) and complexes with various natural (e.g., terrestrial humic substances, phytoplankton metabolites) and anthropogenic (e.g., EDTA, NTA) ligands [43]. Nickel exists in river waters half as ionic and half as stable complexes with humic acids whereas seawater contains Ni mainly as Ni^{2+} , and chloro- and carbonato- complexes. The concentrations in surface water of $15\text{--}20\text{ ng ml}^{-1}$ are measurable directly by GF AAS whereas preconcentration of Ni is absolutely required for seawater ($0.1\text{--}0.5\text{ ng ml}^{-1}$). Direct analysis of seawater with Zeeman AAS offers

TABLE 38.1

Combined procedures for the determination of nickel in waters

Water (amount)	Separation and/or preconcentration	Detection technique	DL (ng/ml)	Ref.
CRM sea (5 ml)	sorption of the bis(carboxy-methyl)dithiocarbamate complex, elution with NH_3aq	ICP MS	0.04	20
CRM sea	volatilization as $\text{Ni}(\text{CO})_4$, trapping on Chromosorb	MIP AES	0.005 ^a	12
CRMs: river, sea	sorption on algae	GF AAS		44
CRMs: sea, river, estuarine (10 ml)	volatilization as $\text{Ni}(\text{CO})_4$, trapping in a graphite furnace	GF AAS	0.004	13
River, spring, lake, coastal (500 ml)	sorption on dioximes loaded naphthalene, dissolution in DMF-HNO_3	FAAS	50	19
River (100 ml)	volatilization as $\text{Ni}(\text{CO})_4$	QF AAS	10 ^a	10
Rain (50 m)	extraction with DDTC (xylene); back-extraction (HNO_3)	GF AAS	0.03	1
Tap, river, ground (3 l)	sorption on Cellex CM, elution with 2 M HNO_3	GF AAS	0.1	18

^a Absolute detection limit, ng.

a DL of 1 ng ml^{-1} [23]. Direct ICP MS with cryogenic desolvation is an alternative [36]. Combined analytical procedures are summarized in Table 38.1. Nickel speciation has been studied by a multi-method approach including chelating resin partitioning followed by GF AAS determination [43].

Clinical samples

The normal Ni levels in serum and blood (*ca* 0.3 ng ml^{-1}) and in urine (2 ng ml^{-1}) can be readily determined by GF AAS which offers detection limits of $0.05\text{--}0.1 \text{ ng ml}^{-1}$ and 0.5 ng ml^{-1} , respectively [25,28–31,45]. Zeeman background correction [9,29–31] is preferred to the D_2 correction [25,28,46]. GF AAS is also recommended for the normal human pulmonary levels [47] and skin depth profiling [26]. The contamination risk is severe. Sample handling in a class 100 environment and acid

TABLE 38.2

Methods for the determination of nickel in clinical materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection technique	DL (ng/g)	Ref.
Plasma (10 ml)	dry ashing, dissoln. in HNO_3	volatn. as $\text{Ni}(\text{CO})_4$	QF AAS	10^a	10
Serum, milk powder	dry ashing or H_2SO_4 - HNO_3 , H_2O_2	anion exchange	RNAA	1	15
Serum, whole blood (15–1000 μl), hair	HNO_3 - HClO_4	volatn. as $\text{Ni}(\text{CO})_4$, trapping on Chromosorb	MIP AES	0.005^a	12
CRM urine	none	sorption of the bis(carboxymethyl)- DTC complex, elution with NH_4OH	ICP MS	0.04	20
CRM urine (0.5 ml)	HNO_3 , H_2O_2	extrn. with bis(trifluoroethyl)- DTC (CH_2Cl_2)	GC-ID MS	n.g.	4
Urine (20 ml)	H_2SO_4 - H_2O_2	volatn. as $\text{Ni}(\text{CO})_4$	MIP AES	1	20
Urine	none	volatn. as $\text{Ni}(\text{CO})_4$, trapping on Chromosorb	MIP AES	0.005^a	12
Urine (1 ml)	HNO_3 , HClO_4	pptn. with APDC, dissoln. in MIBK	GF AAS	n.g.	21
Urine (10 ml)	acidified with HNO_3	volatn. as $\text{Ni}(\text{CO})_4$	QF AAS	10^a	10

^a Absolute detection limit, ng.

leaching of all the material coming in contact with the sample are mandatory [29]. Cu–Be alloyed knives have been exclusively used to collect the samples [31]. Each lot of reagents should be evaluated for Ni content before use [31] but blanks cannot generally be avoided even from the Suprasil quartz [15]. Determination of Ni in clinical materials has been critically reviewed [48]. Combined procedures for the clinical samples are summarized in Table 38.2. Attempts to determine Ni speciation have been rare. In urine only one of two signals was identified as chloride [11].

TABLE 38.3

Determination of Ni in biological certified reference materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/ml)	Ref.
Plant, animal tissues	HNO ₃ , H ₂ O ₂	anion exchange from 9 M HCl	RNAA	1–1.3 ^a	14, 15
Plant (3 g)	HNO ₃ –HClO ₄ –H ₂ O ₂	sorption on dioximes loaded naphthalene, dissoln. in DMF–HNO ₃	FAAS	ca. 50 ^b	19
Plants, animal tissues (0.2 g)	HNO ₃ –HCl (microwave assisted)	extrn. with 1,5- <i>bis</i> (phenyl-2-pyridylmethylene)-thiohydrazide (MIBK)	GF AAS	0.2	9
Plants, animal tissues, urine (0.2 g)	HNO ₃ –HCl (microwave assisted)	extrn. with 1,5-bis(di-2-pyridylmethylene)thiohydrazide (MIBK)	GF AAS	0.2	8
Leaves (1 g)	HNO ₃ –HClO ₄	sorption on Chelex 100	ID ICP MS	n.g.	17
Plants, animal tissues, urine (0.2 g)	HNO ₃ –HCl (microwave assisted)	extrn. with 1,5-bis(di-2-pyridylmethylene)thiohydrazide (MIBK, butanol)	ICP AES	0.5–3 ^b	6–8
Miscellaneous (0.2–0.5 g)	HNO ₃ , HClO ₄	pptn. with APDC, dissoln. in MIBK	GF AAS	n.g.	21
Fish, lobster tissue (0.5 g)	HNO ₃ –H ₂ O ₂	volatn. as Ni(CO) ₄ , trapping in a graphite furnace	GF AAS	0.004	13
Plants, liver (1 g)	dry ashing, dissoln. in HNO ₃ –HClO ₄	volatn. as Ni(CO) ₄	QF AAS	10 ^a	10

^a Absolute detection limit, ng; ^b in the solution fed.

Other biomaterials

Nickel was determined in a variety of CRMs for which the combined procedure developed are summarized in Table 38.3. A possible relationship between soil and vegetable content has been demonstrated by GF AAS [49]. Results of a collaborative study on the direct determination in oils and fats by GF AAS have been presented [6,24,50]. Direct determination of Ni in margarine has been reported [51].

TABLE 38.4

Methods for speciation analysis of nickel

Species	Matrix	Separation technique	Detection	Ref.
Porphyrins	crude oil, gasoline	capillary GC	MIP AES	55
Porphyrins	oil shale	capillary GC	MS	56
Ni-DDTC	water, sediments	high temperature capillary GC	ICP MS	57
Porphyrins	coals, oil shale	high temperature capillary GC	ICP MS	58
Porphyrins	crude oils	high temperature capillary GC	MIP AES	59
Porphyrins	sediments extracts ^a	reversed phase HPLC	VIS	60
Porphyrin and non-porphyrin complexes	heavy crude petroleums, asphaltenes	reversed phase HPLC	GF AAS	61
Thioneins	soy bean flour extracts	electrophoresis	FAAS	62
Thioneins	protein extracts of bean seeds	ultrafiltration	GF AAS	63
	urine	reversed phase HPLC, <i>on-line</i> generation of Ni(CO) ₄	MIP AES	11
Ni-complexes	oil	size-exclusion chromatography	ICP AES	64

^a Sediments extracted with toluene–MeOH followed by CHCl₃–MeOH.

Crude oils

A rapid procedure for the determination of Ni in heavy crude oils on emulsification with water by ICP AES has been developed; aqueous standards matched with emulsifier content have been used for calibration [52]. A direct FAAS method for the determination of Ni in fuel oils has been developed and validated by NAA, GF AAS, ICP AES, ICP MS and XRF in a round-robin test involving 54 laboratories [53]. Separation of nickel alkylporphyrins by RP HPLC has been discussed [54]. Methods for the speciation of Ni are summarized in Table 38.4.

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Niobium

Niobium (Nb, atomic weight 92.9, melting point 2470°C , $d = 8.6 \text{ g cm}^{-3}$) is a grey, lustrous, malleable metal. Natural ^{93}Nb occurs in the earth's crust with an average abundance of 24 ppm, primarily in niobite (columbite). The ^{95}Nb nuclide originates from nuclear fallout and occurs in seawater and may accumulate in marine fauna [1]. The metal is attacked by hot concentrated HCl or H_2SO_4 , and by fuming HNO_3 . It is dissolved in HF (with formation of heptafluoronibate, NbF_7^{2-}). Alkaline fusion produces orthoniobate, NbO_4^{3-} . The major oxidation state of Nb is V. In the absence of complexing agents Nb hydrolyzes over the pH range 0–14. Niobium forms stable complexes with fluoride, oxalate, tartrate and peroxide. Solution analytical chemistry of Nb is difficult since complexing agents which are necessary to keep the element in solution may also hamper its chemical reactions. The only need for the trace Nb determination is related to geological materials.

39.1 SEPARATION AND PRECONCENTRATION

Coprecipitation

During heating acid solutions free of complexing agents Nb hydrolyzes and coagulates to form hydrous oxides which are readily collected by $\text{Zr}(\text{OH})_4$, $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ in acid, neutral and alkaline solutions, respectively. Niobium can be precipitated from solutions containing not too much oxalate, tartrate or EDTA as a compound with cupferron [2], 8-hydroxyquinoline [3] or phenylfluorone (in the presence of Zephiramine) [4] with various collectors, e.g. $\text{Fe}(\text{III})$ or Zr.

Extraction

Extraction of the Nb fluoride complex with oxygen-containing sol-

vents (e.g. MIBK, DIPE, cyclohexanone) is a convenient method for the separation of Nb from Ti, Zr, Sn, Mo, U, W and Fe, and, by a careful optimization of the operating conditions, from Ta. Niobium can be stripped from the organic phase with H_2O_2 . Extraction of Nb from HF solution with *N*-benzoyl-*N*-phenylhydroxylamine [5], *N*-*p*-methoxyphenyl-2-furylacrylohydroxamic acid [6] or α -benzoinoxime [7] into CHCl_3 is fairly selective for Nb (Mo, W and Ta are usually coextracted).

Chromatographic methods

Niobium can be separated on anion and cation exchangers, usually as the fluoride or peroxide complex. Reversed-phase HPLC determination as the 5-Br-PADAP complex from tartrate media has been reported [8].

39.2 DETERMINATION TECHNIQUES

Spectrophotometry and fluorometry

The most popular methods are based on the Nb complexes with thiocyanate ($\epsilon = 2.5 \times 10^4$ at 385 nm) or with azoreagents, e.g. PAR [6] or 5-Br-PADAP ($\epsilon = 7.4 \times 10^4$) [9]. Uranium, V and Ta usually interfere and a preliminary separation of Nb is required. Sensitivity can be increased by flotation of the ion pair of the anionic 3,5-dinitrocatechol Nb complex with Rhodamine B [7] or solid-phase spectrophotometry [3]. Fluorescence of the Nb complexes with morin or quercetin in acidic micellar media (CTA) allowed for the determination of Nb down to the low ng/ml level [10].

Atomic absorption spectrometry,

Atomic absorption spectrometry, especially GF AAS is generally not suitable for trace Nb determination owing to the refractory character of the element and the formation of refractory carbides. Flame AAS using an $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame gives a poor sensitivity of $15 \mu\text{g ml}^{-1}$ at the most sensitive 334.4 and 334.9 nm lines. The sensitivity can be improved by extraction of Nb chelates into MIBK and feeding the organic phase into the flame [6].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers DLs of $50\text{--}100 \text{ ng ml}^{-1}$ at several lines, e.g. 316.340 nm, 271.6 nm and 269.71 nm [2,11]. Spectral lines and coincidences have been comprehensively discussed [12]. Laser ablation ICP AES of rocks was reported to give a DL of $5.6 \mu\text{g g}^{-1}$ [13].

Inductively coupled plasma mass spectrometry

The only natural nuclide ^{93}Nb is overlapped by the $^{56}\text{Fe}^{37}\text{Cl}^+$ ion so Fe and chloride in the final solution should be avoided [2]. The suppression of the Nb signal by U and Al matrices can be compensated for by internal standardization with Ru [2].

39.3 ANALYSIS OF REAL SAMPLES

Alkaline fusion [2] and acid attack with HF-containing mixtures [3,5,7–9,14] are used for sample decomposition. When an alkaline melt is leached, Nb remains in the residue while W, Mo, V and Re pass into the aqueous solution. Some fluxes, e.g. $\text{K}_2\text{B}_4\text{O}_7$, have been reported to be contaminated with Nb [2]. X-ray fluorescence is the predominant analytical technique and offers a DL of $1\text{--}2\ \mu\text{g g}^{-1}$ [15–18]. Trace levels of Nb are neither essential nor toxic so there is almost no work related to the analysis of biomaterials [19]. Niobium occurs in seawater as $\text{Nb}(\text{OH})_6^-$ [19]. The radioactive ^{95}Nb is determined by radiometric techniques after complex ion exchange purification [1]. Analytical methods for the determination of Nb are summarized in Table 39.1.

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TABLE 39.1

Analytical methods for the determination of Nb

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. in HCl-HF	copptn. with cupferron	ICP MS	0.02	2
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. with HCl-HF	copptn. with cupferron	ICP AES	2.5	2
GeoCRMs (0.1 g)	$\text{HNO}_3\text{-HF}$	matrix removal by evaporation of SiF_4	ICP MS	0.04	14
GeoCRMs (0.5 g)	HF-HClO_4 , HCl	HPLC of the 5-Br- PADAP complex	VIS	0.22 ^a	8
GeoCRMs (0.1–1 g)	HNO_3 , HF (microwave assisted)	extrn. with BPHA (CHCl_3)	ICP MS	0.08 ^a	5
GeoCRMs (0.03–0.5 g)	HNO_3 , $\text{HClO}_4\text{-HF}$	extrn. with α -benzo- inoxime (CHCl_3); flotation with 3, 5- dinitrocatechol and Rhodamine B (cyclohexane)	VIS	7 ^a	7
CRM titanium	HCl-HF	anion exchange, copptn. of $^{93\text{m}}\text{Mo}$ with α -benzoinoxime	RPAA	0.4	20
Rocks	$\text{HF-HNO}_3\text{-}$ H_2SO_4 , HCl-HF	copptn. as 8-hydr- oxy-quinolate with Fe	solid-phase VIS	5 ^b	3
Steel, apatite (0.25 g)	HF , HCl	extrn. with α - benzoinoxime	VIS		9

^a ng/ml, in the solution fed; ^b absolute detection limit, ng; RPAA = radiochemical proton activation analysis.

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Osmium

Osmium (Os, atomic weight 190.2, melting point 3050°C, $d = 22.6 \text{ g cm}^{-3}$) is a white metal, the heaviest of the Pt group elements. It occurs in the earth's crust with an average abundance of 1 ppb and accompanies Pt ores, especially those with high contents of Ir and Ru. Osmium sponge is corroded slowly by hot HNO_3 . Finely divided Os dissolves in alkaline hypochlorite solution. The metal is readily dissolved in fused alkalis containing an oxidizing agent (e.g., Na_2O_2) to form the osmate, OsO_4^{2-} , which, on dissolution of the melt in acid, disproportionates into OsO_4 and Os(IV). Osmium exists typically in oxidation states of III, IV, VI and VIII. When osmium solutions are heated with oxidants, OsO_4 is liberated. Osmium(IV) forms halide complexes. Osmium is reduced to the metal by Zn and Sn(II) but usually not quantitatively. Various aspects of the analytical chemistry of Os have been discussed [1–4]. The need for trace analysis is particularly acute in geochronology where the formation of ^{187}Os by β -decay of ^{187}Re ($t_{1/2} = 1.52 \times 10^{11}$ years) offers an opportunity to study the age of ore deposits and extraterrestrial samples.

40.1 SEPARATION AND PRECONCENTRATION

Volatilization

Osmium is effectively separated by distillation of the volatile OsO_4 (boiling point 130°C) from a H_2SO_4 or HNO_3 medium in the presence of $\text{K}_2\text{Cr}_2\text{O}_7$ [5,6], KMnO_4 [7,8], $\text{Ce}(\text{SO}_4)_2$ [8,9], H_2O_2 [6,10,11] or HClO_4 [12,13] as oxidant. The distilled OsO_4 is absorbed either in acid solutions

containing reductants, e.g. 6 M HCl containing thiourea or thiocyanate, or in alkaline solutions where osmate is formed. Selective distillation of Os, while Ru and Re (which are less readily oxidized) remain in the solution, can be achieved in boiling H_2SO_4 containing H_2O_2 [10] or in 1–2 M HCl containing ClO_3^- [4]. Alternatively, Ru and Os can both be oxidized to RuO_4 and OsO_4 , respectively, with a strong oxidant whereupon Fe(II) is added to reduce the Ru(VIII) and the excess of the oxidant. After HNO_3 (5–6 M) has been added, the OsO_4 is distilled.

Other methods

Osmium tetroxide can be extracted from acid solutions with CHCl_3 or CCl_4 [7]. Iron(II) should be added before the oxidation of Os with HNO_3 to keep Ru in solution. Osmium can be separated from Ru by extraction with diethylether from an SCN^- -HCl medium containing H_2O_2 . Osmium can be reversibly sorbed from dilute HCl by anion exchangers [14], or Chelex 100 [6], apparently as $\text{OsO}_2\text{Cl}_4^{2-}$. Polyether-type polyurethane foam enables separation of Os from Ru from a thiocyanate medium [15]. The chloride [16], 8-hydroxyquinoline [17] and 2-(6-methyl-2-benzothiazolylazo)-5-diethylaminophenol [18] complexes of Os can be separated by LC. The vacuum fire assay procedure has been proposed for preconcentration of micro- and nanogram quantities of Os without volatilization losses [19].

40.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometry of Os has been reviewed [20]. 1,5-Diphenylcarbazide reacts with OsO_4 to form a blue-green complex which can be extracted into MIBK to form the basis of the determination. Ion associates formed by anionic chloride or thiocyanate osmium complexes and basic dyes lead to sensitive flotation–spectrophotometric methods [20, 21]. The methods become specific after distillation of OsO_4 .

Atomic absorption spectrometry

Osmium is best determined in reduced N_2O – C_2H_2 flame at 290.9 nm or 305.9 nm lines with a sensitivity of *ca* $1\ \mu\text{g ml}^{-1}$. The sensitivity at the 290.9 nm line in the air– C_2H_2 flame is *ca* 5 times poorer. GF AAS sensitivity is poor (*ca* 1 ng). Wall atomization and the use of uncoated tubes are recommended but nevertheless the calibration curves tend to be non-linear.

Atomic emission spectrometry

OsO₄ gives relatively strong flame emission in an N₂O–C₂H₂ flame at 442.15 nm, enabling a sensitivity 30 ng ml⁻¹ to be obtained in the aspirated MIBK solution [22]. The Ar plasma is able to ionize *ca* 78% of Os [23]. The osmium II 225.585 line is considered to be the most sensitive. The DLs with solution nebulization vary from 40 ng ml⁻¹ to 1 µg ml⁻¹ owing to uncontrolled speciation of Os fed into the nebulizer [24]. Problems in obtaining stable signals have been reported [25]. Effect of pH on the response has been examined in detail [26]. Discrete batch sparging of OsO₄ fed into the plasma was shown to increase the sensitivity and response stability considerably [24]. Even better results were obtained by using a purge-and-trap method giving a DL of 0.5 pg ml⁻¹ [5]. Sample introduction techniques for the ICP were compared [27].

Mass spectrometry

Osmium has seven naturally occurring isotopes ¹⁸⁴Os (0.02%), ¹⁸⁶Os (1.59%), ¹⁸⁷Os (1.64%), ¹⁸⁸Os (13.27%), ¹⁸⁹Os (16.14%), ¹⁹⁰Os (26.38%) and ¹⁹²Os (40.96%). The very high ionization potential of Os (8.5 V) makes TI MS difficult [11]. Resonance ionization have been MS [9,28] and ICP MS [27,29,30] are the techniques of choice. Osmium isotope ratios were determined using solution nebulization [12,31], vapour generation [29,32] and ETV (with Te matrix modifier) [13,27]. The separation of Os from Re is usually required because of the isobaric overlap elements at mass 187 [9]. Rhenium interference can be monitored using ¹⁸⁵Re. Other overlaps are with ¹⁸⁴W and ¹⁸⁶W and with ¹⁹⁰Pt and ¹⁹²Pt. The separation of Os from the above metals is usually achieved by selective distillation [29]. The accuracy is improved by isotope dilution [33].

Neutron activation analysis

Neutron activation of osmium leads to ^{191m}Os (*t*_{1/2} = 14 h, *E*_γ = 0.047 MeV with its daughters: ¹⁹¹Os (*t*_{1/2} = 16 d, *E*_γ = 0.042 and 0.129 MeV) and ¹⁹³Os (*t*_{1/2} = 31 h, *E*_γ = 0.46 MeV [7,34–39]. The ¹⁹³Os activity is usually measured after chemical separation. Selenium-75 interferes at the 0.129 and 0.139 MeV lines. Losses of Os from standards during irradiation have been reported [34].

40.3 ANALYSIS OF REAL SAMPLES

A possibility of losses is of primary concern when validating a procedure for Os. Another serious source of systematic error is the memory

effect. Osmium appears to be retained on glass more readily than other elements [29,30,32]. Organic greases should not be used in the distillation apparatus as they trap OsO_4 and facilitate its reduction [9]. With solution techniques reproducible results are difficult to obtain as the response is considerably affected by the chemical form of Os (often unpredictable) occurring in solution. The highest sensitivity is achieved by nebulization of OsO_4 in acidic media [26]. When such a solution is nebulized the oxide evaporates in the spray chamber from the droplets and thus it is more efficiently transported into the atomizer than the liquid. Osmium at II, III and IV oxidation states is practically involatile and, in addition, can form polymeric species which dissociate in the atomizer with difficulty.

Quantitative fire assay collection of Os by lead is seriously affected by the flux composition and assay conditions. Appreciable losses of Os occur with basic fluxes and a minimum 25 g lead button size is required. Cupellation should be avoided because of the extreme volatility of OsO_4 . Fire assay with NiS is preferred [6,35–38]; a blank of *ca* 75 pg has been reported [6]. Roasting of samples is generally invalid. All evaporations must be done in the absence of oxidizing agents, even in trace amounts. Use of HClO_4 or *aqua regia* is precluded for nondistillation procedures. The use of a reflux or pressure bombs is recommended to avoid losses. Dissolution of samples in a sealed PTFE bomb at high temperature is problematic as OsO_4 will diffuse through PTFE [9]; rapid sealing of the bomb is required. Ethanol and HCl must be present to reduce Os(VIII), that is released from the matrix, to the stable (and not capable of diffusion) hexachloroosmate. Microwave assisted pressure bomb acid decomposition was found to be a rapid and efficient method for the decomposition of molybdenites [33]. From sediments rich in organic matter osmium was distilled from KMnO_4 ; incomplete distillation was encountered when $\text{Ce}(\text{SO}_4)_2$ (successful for ferromanganese minerals) was used [8]. Fusion with Na_2O_2 alone [10] or with additions of alkali carbonates, hydroxides and borates [7,40] is a valid approach to sample decomposition of osmiridium, chromite and molybdenite ores. Osmium is converted into the water-soluble osmate. Some Os blanks have been reported when Zr crucibles were used [10].

Methods for the trace determination of Os are summarized in Table 40.1.

TABLE 40.1

Determination of osmium in geological materials

Material	Sample decomposition	Separation	Determin. technique	DL (ng/g)	Ref.
Rock, ore (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	RNAA	5	35
Sand, ores, rocks (25–50 g)	NiS fire assay	none	INAA	2–20	36–39
River sediments	NiS fire assay	oxidn. with $\text{Cr}_2\text{O}_7^{2-}$ and then H_2O_2 , twice distilled as OsO_4 , trapped in HBr, anion exchange	ID SIMS	6	
Meteorites (1 g)	HNO_3 –HCl (reflux)	volatn. from H_2SO_4 containing CrO_3 , trapped in NaOH soln.	RNAA	n.g.	34
Rocks (0.5–10 g)	EtOH –HCl–HF (bomb)	oxidn. with Ce^{4+} , volatn. as OsO_4 , trapped in HCl–EtOH	ID RIMS	few	9
Meteorite (10 mg)	<i>aqua regia</i> (bomb)	oxidn. with HClO_4 , volatn. as OsO_4 , trapped in water	ICP MS	0.08 ^a	13
Molybdenite	HNO_3 – H_2SO_4 (microwave assisted, bomb)	oxidn. with $\text{Cr}_2\text{O}_7^{2-}$, volatn. as OsO_4 , trapped in thiourea	ID ICP MS	n.g.	33
Marine sediments (1–2 g)	H_2SO_4 –HF	oxidn with Ce^{4+} , volatn. as OsO_4 , trapped in EtOH–HCl	ICP AES ICP MS	n.g.	8

continued

TABLE 40.1 (continuation)

Material	Sample decomposition	Separation	Determin. technique	DL (ng/g)	Ref.
Rocks (0.15–0.5 g)	fusion with Na_2O_2	oxidn. with H_2O_2 volatiln. as OsO_4 , trapped in NaOH	ID TI MS	n.g.	11
Chondrites, meteorite	fusion with Na_2O_2	oxidn. with H_2O_2 , volatiln. as OsO_4 , trapped in NaOH soln.	ID RI MS	several	10
CRMs coal and rock	fusion with NaOH– Na_2O	extrn. of OsO_4 into CCl_4	NAA	1–9 ^a	7
Rocks (0.5 g)	fusion with LiBO_3	sorption on polyDDTC resin	ICP AES	10–20	40

^a Absolute detection limit, pg.

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Palladium

Palladium (Pd, atomic weight 106.42, melting point 1552°C, $d = 12.0 \text{ g cm}^{-3}$) is a grey, lustrous noble metal, one of the Pt group elements. It occurs in the earth's crust with an average abundance of 10 ppb, usually associated with Sb, As and Se in Ni–Cu ores or native, alloyed with Hg or Au. The metal dissolves in hot conc. HNO_3 , H_2SO_4 and *aqua regia* and, on fusion, in alkali metal hydroxides and peroxides. The usual oxidation state of Pd in its compounds is II; the IV state is less common. Brown–red $\text{Pd}(\text{OH})_2$ precipitates at a pH of *ca* 4 and dissolves in excess alkalis. Palladium(II) forms stable cyanide, halide and ammino complexes. Palladium(II and IV) is reduced in acid media to the metal by formic acid, and less noble metals, e.g., Zn, Mg, Al, Fe and Cu. The demand for trace determination of Pd is particularly high in geology and the mining industry. The release of Pd from automobile catalysts raised ecotoxicological concerns [1]. The analytical chemistry of Pd has been discussed in a number of monographs and review papers [2–5].

41.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of the iodide complex, PdI_4^{2-} , into MIBK is the most common. Iron(III) interferes and must be removed, e.g. by extraction into MIBK from 6 M HCl under which conditions Pd is only very slightly extracted. Then iodide is added to allow the extraction of Pd [6]. Dithizone allows Pt and Pd to be separated from other metals and from each other [7,8]. Extraction of Pd with various oximes [9,10], formazans [11], and thiourea derivatives [12,13] has been reported.

Coprecipitation

Coprecipitation of Pd after reduction to the metal is the most popular. The most common reducing agents include less noble metals, formic acid [14,15] and SnCl_2 [16–18] whereas Te [13,19–21], Hg [22] and Se [23,24] are typical collectors. When an acid solution is boiled with powdered Te, Pd is precipitated quantitatively along with Pt whereas Rh and Ir remain in solution. Coprecipitation with dioximes in the presence of Ni and Cu as collectors is an alternative [14,25–27].

Sorption

The PdCl_4^{2-} complex is effectively retained by anion exchangers from dilute HCl which allows separation of Pd from many metals both on cationites [28] and anionites [29–32]. Various chelating resins have been reported to retain Pd [33–41]. Sorption of Pd or Pd complexes on activated charcoal [42], C_{18} -bonded silica [43,44] and polyurethane foam [39] has been reported. Palladium has been separated by LC as a complex with chloride [30,45], PAN [46], 8-hydroxyquinoline [47], DDTC [48], and aminophenol derivatives [49,50].

41.2 DETERMINATION TECHNIQUES

Spectrophotometry

In an acid (HCl , H_2SO_4) medium containing excess of iodide, Pd forms a red–brown complex, PdI_4^{2-} , which forms the basis for a moderately sensitive ($\epsilon = 1.02 \times 10^4$ at 410 nm) spectrophotometric method. The complex associates with basic dyes leading to more sensitive ($\epsilon \approx 2 \times 10^5$) flotation–spectrophotometric methods [51]. Preliminary extraction of Pd (e.g. with dimethylglyoxime) is used to ensure selectivity. Determination of Pd with dithizone ($\epsilon = 3.55 \times 10^4$ at 635 nm) [7,8] or thio-Michler's ketone ($\epsilon = 1.0 \times 10^5$ at 530 nm) is an alternative; Au, Hg and Pt usually interfere.

Atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.1 \mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 flame (oxidizing, lean, blue) at the most sensitive 244.8 and 247.6 nm lines. The determination of Pd by flame atomization is strongly affected by the composition of the aqueous solution (*aqua regia* or HCl) and by the presence of concomitant ions such as Na^+ or SO_4^{2-} . Mutual interferences with other Pt group metals can also be important. Graphite furnace AAS shows a characteristic mass of 10 pg using

pyrocoated tubes and wall atomization. Solid sampling (cup-in-tube atomizer or slurry) has been proposed for direct GF AAS determination of Pd in silver [52].

Inductively coupled plasma mass spectrometry

Palladium has six stable isotopes, ^{102}Pd , ^{104}Pd , ^{105}Pd , ^{106}Pd , ^{108}Pd and ^{110}Pd , with average abundances of 1.02, 11.14, 22.33, 27.33, 26.46 and 11.72%, respectively. A DL of 0.06 ng ml^{-1} can be obtained with pneumatic nebulization [53-56]. Interferences from $^{88}\text{SrOH}$, ^{90}ZrO and ^{89}YOH on ^{106}Pd , ^{89}YO on ^{105}Pd and ^{92}ZrO on ^{108}Pd have been encountered [42,57]. The interference from Cu can be overcome by measurements at ^{106}Pd or ^{108}Pd rather than ^{105}Pd [55]. The interferences were alleviated by ETV with $\text{Ni}(\text{NO}_3)_2$ as matrix modifier [42,53]. For IDA the ^{105}Pd spike was added [42].

Other techniques

Inductively coupled plasma AES offers a DL of 0.5 ng ml^{-1} at the most sensitive 225.585 and 228.226 nm lines. The presence of spectral interferences with Fe, Co, Ni, Cr and Ti requires prior separation of Pd from the matrix [28,58]. Palladium has been determined in gold by ICP AES after sample dissolution in *aqua regia* [59]. Signal suppression by many metals in DCP AES was alleviated in the presence of La and Li [60]. Neutron activation analysis is based on the reaction $^{108}\text{Pd}(\text{n},\gamma)^{109}\text{Pd}$ ($t_{1/2} = 13.5\text{ h}$, $E_\gamma = 0.087\text{ MeV}$). The sensitivity is moderate (ADL 0.2 ng) and chemical separations are usually required owing to the low γ -ray energy and interference from many elements.

41.3 ANALYSIS OF REAL SAMPLES

Environmental materials

Dust accumulating along freeways and busy streets can concentrate up to 0.5 ppm of Pd [1,61]. Samples are collected on filters which are then decomposed with *aqua regia*- HClO_4 -HF. The soot should be removed prior to digestion. The concentrations of Pd in sea and fresh waters are apparently very low, *ca* 40 pg l^{-1} and require multistep and error-prone preconcentration procedures. Picogram levels of Pd were preconcentrated as PdCl_4^{2-} on an anionite, refocused on elution on a single ion-exchange bead and determined by GF AAS [61]. The recovery varied from sample to sample. The stability of Pd solution was tested; the analyte is rapidly lost in deionized water but is stable in 0.1 M HCl for 14 days [42]. Methods for the Pd determination in water are sum-

TABLE 41.1

Methods for the determination of palladium in water

Sample (amount)	Separation/ preconcentration	Determination technique	DL (ng/l)	Ref.
River water	coprecipitation with Se	GF AAS	1 ^a	24
Freshwater (1 l)	sorption on activated charcoal	ICP MS	0.8	42
		ETV ICP MS	0.3	
Seawater	copptn. with α -benzildioxime	NAA	10 ^b	25
Seawater (2.5 l)	matrix removal by cation exchange; anion exchange	ID TI MS	4	62
Seawater (660–1680 l)	precipitation as sulphide with Bi carrier	NAA	0.08	63

^a In the solution analyzed, ng/ml; ^b ADL, ng.

marized in Table 41.1. Examples of the use of Pd in biogeochemical prospecting are scarce [55,64].

Geological materials

In the classical fire assay Pd is readily collected by lead and appears quantitatively in the Ag or Au cupellation bead [65,66]. The nickel sulphide fire assay is recommended for the determination of Pd in sulphide materials, chromite ores, concentrates and mattes [53,67–71]. Palladium from the NiS button may adhere to the walls of the grinding wheel [68]. Elimination of the blank in the NiS fire assay has been discussed [72]. Generally, Pd is leached with *aqua regia* [29,56] and a mixture of *aqua regia* with HF [24,31] more readily than any other Pt group metal but, nevertheless, some minerals (cooperite, braggite) remain unattacked [56]. Only a small fraction of Pd is also leached from chromites, in which it is built into the crystal lattice. Gold, Sb, Ni and Cu are leached together with Pd. Prior to leaching, roasting or attack with an oxidizing mixture containing HF is recommended to degrade sulphides and the silicate matrix. Fusion of the residue after leaching is often practised to ensure quantitative transfer Pd to the analytical solution [20,23,28,35]. Other methods for the sample decomposition involve fusion with alkali fluxes, usually Na₂O₂. In terms of detection techniques ICP MS is gaining popularity with a DL of 0.5–1 ng g⁻¹ ready to be achieved [54]. Recent methods for the determination of Pt in geological materials are summarized in Table 41.2.

TABLE 41.2

Determination of palladium in geological materials

Material (amount)	Sample decomposition	Separation/ preconcentration	Determin. technique	DL (ng/g)	Ref.
Rocks (15 g)	lead fire assay	cupellation in an Au bead	GF AAS	0.2	65
Rocks (10 g)	lead fire assay	cupellation in an Au bead	GF AAS	n.g.	66
Rock, ore (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	NAA	7	19
Rocks	NiS fire assay, the bead dissolved in HCl	none	ID ETV ICP MS	n.g.	53
Rock, ore (25 g)	NiS fire assay	none	INAA	25	70
CRMs (10 g)	NiS fire assay	none	GF AAS		68
CRMs (20–30 g)	NiS fire assay	none	ICP MS	ca 0.1	71
Ores (50 g)	NiS fire assay	none	GF AAS	1 ^a	69
CRMs (0.5 g)	HCl–HNO ₃	copptn. with Hg	GF AAS	n.g.	22
Rocks	HF–HNO ₃ (bomb)	SPE on poly(vinyl- thiopropionamide) resin, elution thiourea, 1 M HCl	GF AAS	n.g.	37
CRMs (0.5–1 g)	HF–HCl–HNO ₃ , HClO ₄	pptn. with α - benzildioxime	NAA	10 ^c	25
Rocks (0.3–4 g)	HF–HClO ₄ – H ₂ SO ₄ (bomb)	anion exchange or copptn. with Te or extrn. with N,N- diethyl-N'- benzoylthiourea	AAS	n.g.	13
Rocks (5 g)	HF– <i>aqua regia</i> (bomb)	anion exchange	GF AAS	2	31
Rocks, soils (0.5 g)	HNO ₃ –HCl– HClO ₄ , <i>aqua regia</i>	extrn. of PdI ₄ ²⁻ (MIBK)	GF AAS	3	6
Rocks (0.5–1.5 g)	<i>aqua regia</i> , HF– HClO ₄ (bomb)	copptn. with Se	GF AAS	1 ^a	24

continued

TABLE 41.2 (continuation)

Material (amount)	Sample decomposition	Separation/preconcentration	Determin. technique	DL (ng/g)	Ref.
Mn crust (0.25 g)	<i>aqua regia</i> -HF	copptn. with Se	GF AAS	1 ^a	24
CRM (4 g)	<i>aqua regia</i> , fusion with Na ₂ O ₂	copptn. with Te	DCP AES	n.g.	73
CRM (2.5 g)	<i>aqua regia</i>	anion exchange of PdCl ₄ ²⁻ , ashing of the resin	GF AAS	10	29
Rocks (10 g)	<i>aqua regia</i>		ICP MS	n.g.	56
Ores	<i>aqua regia</i> , HF-HNO ₃ -HClO ₄ , the residue fused with Na ₂ O ₂	cation exchange, PdCl ₄ ²⁻ not retained	ICP AES	4 ^b	28
Ores (2 g), rocks (5 g)	<i>aqua regia</i> -HF, the residue fused with Na ₂ O ₂	copptn. with Te	GF AAS	7 ^d	20
Rocks (5 g)	roasting, H ₂ SO ₄ -HF; fusion with Na ₂ O ₂ -KHCO ₃	copptn. with Se	GF AAS	0.5	23
Sulphide ores (2.5 g)	roasting, <i>aqua regia</i> , the residue fused with Na ₂ O ₂	sorption on dehydro-dithizone column, elution with thiourea	DCP AES	n.g.	35
Rocks (0.2 g)	fusion with Na ₂ O ₂ -NaOH	extrn. with N,N'-dibenzylthiooxamide	NAA	0.02	74
Rocks	fusion with Na ₂ O ₂ -NaOH	copptn. with Te	NAA	0.01	16
Rocks (1 g)	fusion with Na ₂ O ₂	extrn. with N,N'-diphenylthiourea or TPP (1,2-dichloroethane)	ICP AES	20 ^b	12
Pt ore (0.5 g)	fusion with LiBO ₂	sorption on polyDDTC resin, then digested by 50% H ₂ O ₂	ICP AES	900	33

^a ng/ml in the solution analyzed; ^b µg/ml in the solution fed; ^c absolute detection limit, ng; ^d characteristic mass, pg.

Industrial materials

These include intermediates and by-products in industrial production of Pd from ores, sweeps, alloys and jewellery, and catalysts. Fusion attack with Na_2O_2 , either direct or after leaching, is almost always required for concentrates, slags and mattes [15,20,35]. Flame AAS and ICP AES are the usual techniques used. Catalysts can be treated in a way similar to that described for Pt (*cf.* Chapter 42). Direct methods are preferred. Methods for the determination of Pd in industrial materials are summarized in Table 41.3.

TABLE 41.3

Methods for the determination of palladium in industrial materials

Material (amount)	Sample decomposition	Separation/preconcentration	Determin. technique	DL	Ref.
Concentrate	HCl	anion exchange, LC	UV	10 ^a	30
Sweeps	fusion with Na_2CO_3 and Na_2O_2	pptn. with formic acid, dissoln. in <i>aqua regia</i>	AAS ICP AES DCP AES	0.1 ^b	14
Sweeps	NiS fire assay, dissoln. in HCl, <i>aqua regia</i>	none	AAS ICP AES DCP AES	0.1 ^b	14
Concentrates, mattes (2.5 g)	<i>aqua regia</i> , the residue fused with Na_2O_2	sorption on dehydrodithizone column, elution with thiourea	DCP AES	n.g.	35
Concentrate	lead fire assay, dissoln. in HClO_4 -AcOH	pptn. with formic acid, dissoln. in <i>aqua regia</i>	FAAS	5 ^b	14
Concentrates, mattes (2 g)	<i>aqua regia</i> -HF, the residue fused with Na_2O_2	copptn. with Te	GF AAS	7 ^c	20
Concentrates	<i>aqua regia</i> , HF- HNO_3 - HClO_4 , the residue fused with Na_2O_2	cation exchange, PdCl_4^{2-} not retained	ICP AES	4 ^d	28

^a ppb in the solution analyzed; ^b ppm in the sample; ^c characteristic mass, pg; ^d ppm in the solution analyzed.

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Platinum

Platinum (Pt, atomic weight 195.09, melting point 1769°C, $d = 21.45 \text{ g cm}^{-3}$) is a silvery-grey, malleable noble metal. It occurs in the earth's crust largely dispersed with an average abundance of 5 ppb. The metal dissolves in *aqua regia* with the formation of PtCl_6^{2-} and in fused alkalis containing an oxidant (e.g. Na_2O_2 or NaNO_3). The principal oxidation states of Pt are II and IV, the latter being more stable. Alkalis precipitate from aqueous solutions of Pt(IV) the hydroxide, $\text{Pt}(\text{OH})_4$, which dissolves in the excess of the reagent. Hydrogen sulphide precipitates from dilute HCl dark brown sulphide, PtS_2 , which dissolves in a Na_2S or $(\text{NH}_4)_2\text{S}$ solution forming the complex PtS_3^{2-} . Platinum forms thermodynamically stable but kinetically inert halide, pseudo-halide and ammino complexes. Platinum(IV) is reduced to the metal by Zn, Mg, Al and formic acid. Trace analysis for Pt is primarily demanded in geology and mining industry. Soluble Pt compounds are toxic and chronic industrial exposure to them is responsible for a syndrome called platinosis. Some Pt compounds are used in chemotherapy of cancer and need to be monitored in clinical samples. The release of Pt from automobile catalysts raised ecotoxicological concerns.

42.1 SEPARATION AND PRECONCENTRATION

The complex solution chemistry of Pt with important kinetic effects makes wet separation–preconcentration methods error prone and requires an experienced analyst [1–4].

Extraction

Chloride, bromide and iodide complexes are commonly used for the extraction separation of Pt. Iron(III) interferes and must be removed,

e.g. by extraction into MIBK from 6 M HCl, under which conditions Pt is only very slightly extracted. Then iodide is added to extract Pt [5]. S-donor organic reagents, e.g. dithizone [6-9] or 2-mercaptobenzothiazole [10] are a common alternative. The extraction is often carried out in the presence of SnCl_3^- acting as a labilizing agent [11]. Extraction of Pt(IV) from various systems has been carefully investigated by means of ^{191}Pt radiotracer [12].

Coprecipitation

Coprecipitation of Pt upon reduction to the metal in dilute acid is popular. Electronegative metals (Zn, Mg, Fe), hydrazine, formic acid [13] and SnCl_2 [14] are the most common reductors whereas Te [15-18], Hg [19] and Se [20,21] are widely employed as collectors. When an acid solution is boiled with Te powder, Pt and Pd are precipitated quantitatively whereas Rh and Ir remain in solution. Platinum can be separated by precipitation as sulphide (by H_2S or thioacetamide) or as a compound with thiourea or 2-mercaptobenzothiazole in the presence of Cu and Ni as collectors [22]. Electrodeposition of Pt on a graphite tube has been developed [23].

Sorption and ion exchange

The PtCl_6^{2-} (and PtBr_6^{2-}) complex is strongly sorbed by anion exchangers in dilute acid which allows separation from many non-noble metals by means of both cation [24-26] and anion [27-31] exchangers. Sorption of Pt on chelating resins [32-38] is widely used. Other sorbents included C_{18} silica [39-41], alumina [42] and activated charcoal [43]. Polyether type polyurethane foam retain Pt(II) and Pt(IV) on reduction to Pt(II) quantitatively from dilute HCl in the presence of Sn(II) chloride [44,45]. Liquid chromatographic separation of Pt as the PAN complex [46], 8-oxinate [47], diethyldithiocarbamate [48] or chloro complexes [49] has been discussed.

42.2 DETERMINATION TECHNIQUES

Spectrophotometry

The most popular is the method based on the reaction of SnCl_2 with Pt(IV) in dilute HCl to produce a yellow-orange complex ($\epsilon = 1.3 \times 10^4$ at 403 nm) which is extractable into oxygen-containing solvents. Rhodium and Pd interfere. The $\text{Pt}(\text{SnCl}_3)_4^{2-}$ complex may form ion pairs with basic

dyes that form the basis of sensitive ($\epsilon \sim 3 \times 10^5$) flotation-spectrophotometric methods [50]. Dithizone reacts with Pt(II) in 1–4 M HCl or H_2SO_4 medium in the presence of Sn(II) forming the brown-yellow dithizonate $\text{Pt}(\text{HDz})_2$ soluble in CCl_4 or CHCl_3 ($\epsilon = 3.75 \times 10^4$ at 490 nm) [7,8]. The significance of catalytic methods is minimal [51].

Atomic absorption spectrometry

Flame AAS offers a poor sensitivity of $0.5 \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame at the 265.9 nm line and is seldom used in trace analysis for Pt. The refractory character of Pt is also responsible for some drawbacks in electrothermal AAS. The absolute detection limit is about 30 pg. The atomization from the wall is strongly preferred to that from the platform. The use of maximum power heating, use of gas stop during the atomization step and peak area measurement with baseline offset control are essential to produce reliable results. The high pyrolysis temperature (1400–1800°C) allows effective removal of organic and alkali metal chlorides prior to atomization. Elemental interferences have been discussed [52]. Solid sampling using cup-in-tube atomizer and slurry were compared for direct GF AAS determination of Pt in silver [53].

Neutron activation analysis

Neutron activation analysis is based on the reaction $^{198}\text{Pt}(n,\gamma)^{199}\text{Pt} \rightarrow ^{199}\text{Au}$ and counting the ^{199}Au γ -peak ($t_{1/2} = 3.15$, $E_\gamma = 0.158$ MeV) [54,55]. The principal interference results from the formation of ^{199}Au via reaction: $^{198}\text{Au}(n,\gamma)^{199}\text{Au}$ in an amount equivalent to 2.4 ng Pt per nanogram of ^{198}Au in the sample. A correction must be applied. The DL of 0.3 ng is adversely affected by the Au sample content owing to the uncertainty in the correction for the ^{199}Au contribution. Effective ADLs are rather high: 1–10 ng. The produced Au is separated electrolytically [56,57]. Other interferences include a γ -peak 0.160 MeV from ^{47}Sc being the daughter radionuclide of ^{47}Ca ($t_{1/2} = 4.7$ d) and the background from ^{32}P . The latter can be eliminated by separation of the interfering nuclide on an acid alumina column.

Mass spectrometry

Platinum has six stable isotopes, ^{190}Pt (0.01%), ^{192}Pt (0.78%), ^{194}Pt (32.9%), ^{195}Pt (33.8%), ^{196}Pt (25.2%) and ^{198}Pt (7.19%), and thus it is readily amenable to IDA. ICP MS offers DL down to the ppt level [58,59]. ^{194}Pt and ^{195}Pt are usually monitored [43,60]; the ^{194}Pt is used

as the spike [43]. Alternatively ^{192}Pt can be used as a spike, $^{192}\text{Pt}/^{194}\text{Pt}$ has been measured [27]. Matrix related interferences can be removed by using electrothermal vaporization [43,61]. The major spectral interference is the overlapping of all major Pt isotope signals (194, 195, 196 m/z) by HfO_2 which is considerably more abundant (*ca* 300 times) in the earth's crust than Pt making a related separation mandatory. Cation [62] and anion [27] exchange have been proposed. The volatility of Pt chelate with bis(trifluoroethyl)dithiocarbamate makes GC ID MS possible [66].

Other techniques

The potential of rapid analysis by XRF is utilized in routine quality control in the manufacture of catalysts [64]. ICP AES offers a DL of $0.03 \mu\text{g ml}^{-1}$ at the most intensive line 214.423 nm that is interfered with by Al and Fe. Other lines, 203.646 and 265.945 nm, have been used [18] but separation of Pt prior to analysis is required [65].

42.3 ANALYSIS OF REAL SAMPLES

Environmental samples

The analysis of airborne particulate matter is stimulated by the release of Pt from automotive catalysts [52,62,63]. Samples are collected on filters which are then wet ashed with *aqua regia*– HClO_4 –HF. This acid digestion may be ineffective for the dissolution of PtO_2 . The latter is converted on heating at 400°C to PtO and Pt^0 which are both soluble in *aqua regia*. Further, the soot in vehicle exhaust particulates should be removed prior to digestion. Little is known on the presence of Pt in sea and fresh waters. In recent works concentrations between 0.4 and 1.7 pM have been determined. Platinum in fresh water is retained on charcoal [43] and in seawater by anion exchange resin [27]. Picogram levels of Pt are preconcentrated from water samples as the anionic chloride complex on ion-exchange resins. Platinum was eluted from the column and purified by adsorption onto a single ion-exchange bead, then stripped from the bead and determined by means of a GF AAS; the recovery varied from sample to sample [30].

Geological materials

The carriers of platinum in basic rocks (containing chromite and Cu sulphides) are mostly very finely dispersed forms of natural alloys

(Pt-Fe), sulphides, tellurides and arsenides. Because of the malleability of the alloys, there may be some loss when a sample is pulverized to 200 mesh. Lead fire assay ensures quantitative collection of Pt in the button but a 20-fold excess of silver is required to prevent losses of Pt during cupellation. The cupellation step can be avoided by parting the lead button with HClO_4 -acetic acid and precipitating Pt by 2-mercaptobenzothiazole or thiobarbituric acid or as metal by heating with formic acid. Silver is separated as AgClO_4 on standing [13]. The nickel sulphide fire assay is recommended for the determination of Pt in sulphide and chromite ores [15,61,67,68]. An alternative is leaching with *aqua regia* after degrading sulphides and the basic matrix by roasting or attack with HF-containing oxidizing mixture. Fusion of the residue after leaching is often practised to ensure quantitative transfer Pt to the solution [24]. Fusion with Na_2O_2 is recommended for chromites in which Pt exists built into the lattice. Recent methods for the determination of Pt in geological materials are summarized in Table 42.1.

Biological materials

The levels of Pt in body fluids after administration of the drugs are $0.1\text{--}10\text{ }\mu\text{g g}^{-1}$ and are easily accessed by direct GF AAS [71], ICP AES [72] and ICP MS [73]. The analysis for the natural Pt levels which are *ca* three orders of magnitude lower requires combined procedures. Dry ashing at $800\text{--}900^\circ\text{C}$ is allowed but at higher temperatures losses of Pt are observed. In one work, however, unexplained losses of Pt when dry ashed in a furnace were found [74]. The mineralized residue is dissolved in *aqua regia*. In the wet decomposition method tissues are dissolved in hyamine hydroxide at $50\text{--}60^\circ\text{C}$ overnight [75] or digested with HNO_3 -*aqua regia* [11,17,19]. Hydrogen peroxide is added to destroy lipid material [63,74]. Iron and NaCl as well as HNO_3 depress the AAS signal of Pt. Graphite furnace AAS after extraction is the most typical but ICP MS is rapidly gaining popularity [60]. Procedures for the determination of Pt in biomaterials are summarized in Table 42.2.

Industrial materials

Concentrates, slags and mattes differ from geological material mostly in terms of a higher Pt content and more difficult decomposition. Fusion attack with Na_2O_2 , either direct or after leaching, is almost always required [16,24,35]. The large dynamic range of ICP-AES makes this technique particularly suitable for this type of analysis [24]. An alternative technique is the direct determination of Pt by XRF [64].

TABLE 42.1

Determination of platinum in geological materials

Material (amount)	Sample decomposition	Separation	Detection	DL (ng/g)	Ref.
Ores	roasting, lead fire assay, dissoln. in HClO_4 -AcOH	precipitation with formic acid	AAS	35-200 ppm	13
Sand, ore, basalt (25 g)	NiS fire assay	none	INAA	18	67
Rock, ore (20-50 g)	NiS fire assay, the bead dissolved in HCl	coprecipitation with Te	NAA	15	15
Rocks	NiS fire assay, the bead dissolved in HCl	none	ID ETV ICP MS	n.g.	61
Street dust, CRM ore (150-180 mg)	high pressure digestion	sorption on polyurethane foam	RNAA	3.6-20	55
CRM (10 g)	NiS fire assay	none	GF AAS	n.g.	68
CRMs (0.5 g)	HCl-HNO_3	copptn. with Hg	GF AAS	n.g.	19
Rocks, soils (0.5 g)	HNO_3 -HCl- HClO_4 , <i>aqua regia</i>	extn. of PtI_6^{2-} (MIBK)	GF AAS	10	5
CRM (4 g)	<i>aqua regia</i> , the residue fused with Na_2O_2	copptn. with Te	DCP AES	n.g.	18
CRM (2.5 g)	<i>aqua regia</i>	anion exchange of PtCl_6^{2-} , ashing of the resin	GF AAS	20	29
Sediments (0.5-1 g)	HF-HNO_3 (microwave assisted)	anion exchange of PtCl_6^{2-} , elution with 12 M HNO_3	ID ICP MS	14 pg	27
Sulphide ores (2.5 g)	<i>aqua regia</i> , the residue fused with Na_2O_2	SPE on dehydrodithizone column	DCP AES	n.g.	35
Rocks (5 g)	H_2SO_4 -HF, the residue fused with Na_2O_2 -NaKCO ₃	copptn. with Se on reduction of Fe(III) with SnCl_2	GF AAS	2	20

Material (amount)	Sample decomposition	Separation	Detection	DL (ng/g)	Ref.
Ores	<i>aqua regia</i> , HF–HNO ₃ –HClO ₄ , the residue fused with Na ₂ O ₂	cation exchange, PtCl ₆ ²⁻ not retained	ICP AES	50 ^b	24
Ores (2 g), rocks (5 g)	<i>aqua regia</i> –HF, the residue fused with Na ₂ O ₂	copptn. with Te	GF AAS	90 ^d	16
Sediments, nodules (0.5–1 g)	HF–HCl–HClO ₄ the residue fused with Na ₂ O ₂	double-step anion exchange, elution with HCl and thiourea	GF AAS	15 ^c	30
CRMs coal and rock	fusion with NaOH–Na ₂ O, dissoln. in H ₂ SO ₄	cation exchange, PtCl ₆ ²⁻ not retained	NAA	1–9 ^c	26
Pt ore (0.5 g)	fusion with LiBO ₃ , dissoln. in HNO ₃	sorption on polyDDTC resin, then digested with 50% H ₂ O ₂	ICP AES	1.6 ppm	32
Rock (~0.5g)	fusion with Na ₂ O ₂ , lead fire assay	lead button fused with NaOH–Na ₂ O ₂	NAA	3–50	69
Rocks (0.2 g)	fusion with Na ₂ O ₂ –NaOH	reduction of Pt to Pt(II) with SnCl ₂ , extrn. with N,N'-dibenzylidithio-oxamide into CHCl ₃	NAA	0.5	70
Rocks, nodules (0.5–1.5 g)	HNO ₃ –HF (bomb)	copptn. with Se	GF AAS TR XRF	n.g.	21
Rocks (5 g)	HF– <i>aqua regia</i> (bomb)	anion exchange	GF AAS	5	28
Rocks	HNO ₃ –HF (bomb)	SPE on poly(vinyl-thiopropionamide) resin, elution with thiourea, 1 M HCl	GF AAS	n.g.	37
Slag, dust (0.1–2 g)	HNO ₃ –HCl, high pressure	electrodeposition	GF AAS	0.3 ng	23

^b in ppb in solution; ^c absolute detection limit; ^d sensitivity.

TABLE 42.2

Methods for the determination of platinum in biological and clinical materials

Material (amount)	Sample digestion	Separation	Detection	DL (ng/g)	Ref.
Plant (1–2 g ash)	ashing, dissoln. in <i>aqua regia</i>	copptn. with Te	GF AAS, ICP MS	0.5–2	17
Plant (0.4 g)	<i>aqua regia</i> (bomb)	extrn. with dithizone (MIBK)	GF AAS	40	11
Plant (0.5 g)	<i>aqua regia</i> (bomb)	anion exchange	UV photometry	40	31
Plant (0.1–2 g)	HNO ₃ –HCl (bomb)	electrodeposition	GF AAS	0.3 ^b	23
Plant (0.1–2 g)	HNO ₃ –HCl (bomb)	sorption as bis(carboxymethyl)dithio- carbamate complex on XAD-4 resin	GF AAS	0.1 ^a	41
Algae (3–5 g)	HCl–HNO ₃ – HClO ₄	two-step anion exchange, elution with HCl and thiourea	GF AAS	0.015 ^b	30
Plant, animal	HNO ₃ – HClO ₄	extrn. with DDTC	RNAA	few	54
Plant (0.15–0.18 g)	bomb	sorption on polyurethane foam	RNAA	13	55
Animal (0.1–300 g)	HNO ₃	anion exchange of PtCl ₆ ^{2–}	ICP MS	<0.1	77
CRM animal	HCl– HNO ₃ – HClO ₄	separation of Au on Nb cathode	NAA	0.4–1.1	57
Animal	HNO ₃ – HCl–H ₂ SO ₄	pptn. with SnCl ₂	NAA	0.24 ^b	14
Animal	HNO ₃	none	GFAAS, NAA	0.5 ^b	25
Animal	HNO ₃	cation exchange, elution with thiourea	RNAA	0.07 ^b	25

Material (amount)	Sample digestion	Separation	Detection	DL (ng/g)	Ref.
Tissues (liver, muscle)	hyamine hydroxide, dilution with HCl	none	GF AAS	250	75
Plasma, urine, tissue (10 µl)	HNO ₃ – H ₂ O ₂	none	GF AAS	6	74
Serum	HNO ₃	none	ICP MS	0.4	58
Urine	HNO ₃	none	GF AAS	0.4	76
Urine (0.5 ml)	HNO ₃ – H ₃ PO ₄ , H ₂ O ₂	extrn. with Li– (bis(trifluoroethyl) DDTC (CH ₂ Cl ₂)	ID GC/MS	3	63

^a ng/ml in the solution fed; ^b absolute detection limit.

In the analysis of catalysts the main problem is the lack of homogeneity of the materials. A sample of 300 g is required in order to obtain accuracy within 2% in chemical methods of analysis. In practice 10–15 g portions are used. The fire assay may be not able to cope with the high alumina content [3]. The sample is usually leached with *aqua regia* and Pt is precipitated with tellurium. A mixture of H₂O₂ and HCl has yielded good results in leaching platinum deposited on Al₂O₃ (re-forming catalysts). Direct techniques (GD MS or XRF) are preferred [3].

Accuracy considerations

The occurrence at different oxidation steps, the unknown speciation and the kinetic indifference of many complexes considerably reduce the value of recovery studies as a proof of accuracy even in the case of relatively simple matrices. Losses of Pt by sorption to the vessel walls are common when PTFE is used. Nitric acid vapour cleaned quartz has been recommended as the material for ultratrace analysis [11]. Stability of the Pt solutions has been tested; the analyte was rapidly lost from deionized water but was stable in 0.1 M HCl for 14 days [43]. Except for the field of geochemistry, CRMs are practically non-existent.

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Rare earth elements

Rare earth elements (REE) discussed below include yttrium and the lanthanides. The latter constitute a series of 15 elements, 14 of which exist in nature whereas one, promethium (Pr), is an artificial element absent in the earth's crust. Scandium, which is often referred to as a rare earth element, is discussed separately in Chapter 48 owing to different analytical chemical properties. Most REEs are bright, silver-grey, malleable and, generally, soft metals, fairly abundant in the earth's crust, occurring primarily in monazites (as phosphates). Some REE nuclides, e.g. ^{90}Y , ^{91}Y and ^{144}Ce , are products of nuclear fallout. Basic physical properties and the earth crust abundances of the REEs are listed in Table 43.1. The REEs show similar chemical properties. The most common oxidation state is III; Ce, Pr and Tb exist in the IV state whereas Eu, Sm, and Yb may persist in lower (II) state in the presence of strong reductants. In aqueous solution the REEs form triply charged cations. These ions are colourless except Ce^{4+} (yellow), Pr^{3+} (green), Nd^{3+} (red-violet), Sm^{2+} (red-orange), Eu^{2+} (greenish yellow), Er^{3+} (red) and Yb^{2+} (green). At pH above 6–8 (depending on the element) hydroxides are precipitated which are insoluble in excess of alkalis but soluble in mineral acids. The REEs form sparingly soluble fluorides, phosphates, oxalates, carbonates and iodates, and strong complexes with oxo ligands such as EDTA, tartrate, citrate.

Rare earth elements have an increasing variety of industrial applications and have started to become relevant to environmental concerns. Chemistry and toxicology of the REE have been reviewed [1,2]. The REE patterns and isotopic systematics are used in geochemistry as fingerprints of the age and source [3]. REEs are used as sensitive indicators of geochemical processes and are mostly determined in environ-

TABLE 43.1

Physical properties of yttrium and the lanthanides

Element	Symbol	Atomic no.	At. wt.*	M.p. (°C)	<i>d</i> (g cm ⁻³)	Earth crust abundance (ppm)
Yttrium	Y	39	88.91	1509	4.47	28
Lanthanum	La	57	138.91	920	6.17	30
Cerium	Ce	58	140.12	795	6.67	60
Praseodymium	Pr	59	140.91	935	6.77	8.2
Neodymium	Nd	60	144.24	1024	7.00	28
Promethium	Pm	61	145	1080	—	—
Samarium	Sm	62	150.36	1072	7.54	6
Europium	Eu	63	151.96	826	5.26	1.2
Gadolinium	Gd	64	157.25	1312	7.89	5.4
Terbium	Tb	65	158.93	1356	8.27	0.9
Dysprosium	Dy	66	162.50	1407	8.54	3.0
Holmium	Ho	67	164.93	1461	8.80	1.2
Erbium	Er	68	167.26	1497	9.05	2.8
Thulium	Tm	69	168.93	1545	9.33	0.5
Ytterbium	Yb	70	173.04	824	6.98	3.0
Lutetium	Lu	71	174.97	1652	9.84	0.5

*Atomic weight of the most stable isotope.

mental waters and geological materials. The analytical chemistry of REEs has been reviewed [4].

43.1 SEPARATION AND PRECONCENTRATION

Extraction, coprecipitation and sorption are all equally often used for the group separation–preconcentration of the REEs. Radiotracers are recommended to check the chemical yield from real samples to avoid ambiguity [5]. The separation of the REEs from each other is usually achieved by chromatography and has been reviewed [6,7].

Extraction

Extraction of REE as anionic (e.g. nitrate or EDTA) complexes with higher amines into nonpolar solvents is widely used [8,9]. Esters of

phosphoric acid have alternatively been proposed [9–13]. The REE can be stripped with HNO_3 [11] or with H_2O after increasing the polarity of the organic phase [10]. Synergetic extraction of trivalent lanthanides with TTA in the presence of terpyridine [14], dialkyl sulphoxides [15] or ionizable macrocycles [16,17] has been studied. Extraction of REEs with various crown ethers has been investigated in detail [18–22] but only few practical applications have been reported [23]. Supercritical fluid extraction of the lanthanides with fluorinated β -diketones and TBP has been developed [24–26].

Coprecipitation

Coprecipitation of REEs as hydroxides, usually with $\text{Fe}(\text{OH})_3$ [27–32] or $\text{Mg}(\text{OH})_2$ [5] as carriers from neutral and alkaline media, respectively, is the most popular. Better selectivity is obtained by the precipitation of the REEs as oxalates from a weakly acidic medium (pH 1–4) using Ca as a collector [5,33–35]. The coprecipitation of Th is prevented by masking it with EDTA at pH 3.2. In media too acidic for the precipitation of oxalates, the REEs can be separated as fluorides using Ca as collector [36,37] but the yield is poorer and the precipitate is more difficult to filter than in the case of oxalates. Coprecipitation of the REEs with organic reagents, e.g. rhodizonic acid [38,39] or cupferron [40] and as the nitrate complexes on diethylether-loaded cellulose has been reported [41].

Sorption and ion exchange

Sorption of the REEs, especially Ce, on charcoal [42,43] and various (Al, Si, Pb, Fe, Th and Mn) oxides [44,45] has been investigated. The REE were also retained on PAN-modified naphthalene [46] or DDTC impregnated polyurethane foams [47], or as 8-hydroxyquinoline complexes on activated carbon [48]. Low pressure ion exchange is used for the group separation of REEs from alkali, alkaline earth, Sc and transition metals. Cation exchange using HNO_3 and/or HCl as eluents is the most popular [28,29,32,33,36,37,49–57]. The fairly selective retention of the REEs by anion exchangers from HNO_3 –acetate media is less common [39,58]. Sequential cation and anion exchange procedures are used for purification of the REE fraction, especially for TI MS [31].

High-performance liquid chromatography

High-performance liquid chromatography is gaining acceptance for the separation of the REE from each other. Cation-exchange HPLC

using HCl (gradient elution) [59], α -isobutyric acid [60–62] or lactate [40,61] as mobile phases is the most popular. Resolution can be improved by adding ion-pairing reagents, e.g. 1-octanesulphonic acid [62, 63]. The chromatography is often preceded by a preliminary separation of the REEs from alkali and alkaline earth salts [40]. Carrier-mediated transport of REEs through liquid and plasticized membranes has been reviewed [64].

43.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometry is exclusively used for the determination of the total REE content or for the chromatographic detection of REEs [63]. The determination is usually based on the reaction with Arsenazo III in weakly acid media (pH 2–3) which is fairly sensitive ($\epsilon = 5.6 \times 10^4$ at 515 nm). Thorium, Zr, U, Bi and Cu interfere. Other azo dyes, e.g. Arsenazo I, Chlorophosphonazo [65] and PAR [66], can be used alternatively. The determination of the total REE content usually follows a coprecipitation separation step combined with EDTA masking. A repetitive spectral subtraction method was developed [67].

Atomic absorption spectrometry

Atomic absorption spectrometry offers variable performance depending on the metal. The most intensive absorption lines and characteristic concentrations for FAAS and GF AAS are summarized in Table 43.2. The lanthanides exhibit a complex pattern of mutual spectral interferences. Flame AAS is hampered by the formation of thermally stable oxides which, in the cases of La, Pr, Gd and especially Ce, virtually prevent trace analysis. The high temperature $N_2O-C_2H_2$ flame (reducing rich) is recommended for all the REEs. Ionization should be controlled by the addition of an alkali metal salt, e.g. KCl. An enhancement effect of surfactants and organic acids has been observed [68]. Indirect methods based on the enhancement of the atomic signal of Fe by small amounts of Ce and La have been proposed [69]. In addition to the formation of the oxides GF AAS is affected by that of stable carbides [49,70,71]. Optimum ashing and atomization temperatures have been established for all REE except La and Ce [50]. Interferences on Eu, Sm and Tb have been extensively discussed [50]. Pyrolytically coated tubes are essential. The low sensitivity is particularly acute for La, Ce, Pr,

TABLE 43.2

Analytical lines and sensitivity characteristics for AAS determination of REE

Element	Line (nm)	FAAS DL (μg/ml)	GF AAS c.m.* (ng)	Element	Line (nm)	FAAS DL (μg/ml)	GF AAS c.m.* (ng)
Y	410.2	1.6	13 ^a	Gd	368.4 407.9	19	11
La	550.1	50	26 ^a	Tb	432.6	5.9	—
Ce	—	—	—	Dy	404.6 421.2	1.0	0.04 ^a
Pr	495.1	40	—	Ho	410.4 405.4	0.9 1.1	—
Nd	492.4 463.4	7.3	1.8 ^a	Er	400.8	0.7	0.07 ^a
Pm	—	—	—	Tm	371.8 410.6 374.4 409.4	0.4–0.8	0.01 ^a
Sm	429.7	6.7	0.24 ^a	Yb	398.8	0.1	0.003
Eu	459.4	0.7	0.02	Lu	336.0	6.0	—

*c.m. = characteristic mass.

^a Memory effects are important; — no reliable determination was reported.

Gd, Tb and Lu which cannot be reliably determined unless atomized from Ta (or W) lined furnaces [49,71,72] or Ta boats [70]. Holmium, Sm, Er and Dy can be determined provided that the method of standard additions is used for calibration [50]. Vaporization of Dy in a graphite furnace has been studied in detail [73]. Europium, Tm and especially Yb can be relatively easily determined by ETA AAS. Except for the case of the uncoated graphite tube, the detection characteristics for Yb were found to be similar for pyrocoated graphite, metal carbide and metal-coated tubes (DL of 5–15 ng ml⁻¹) [74]. A characteristic mass of 1 pg for Yb was reported using a Ta-lined atomizer [75,76]. A simultaneous multielement GF AAS of the REEs has been developed [77].

Atomic emission spectrometry

The most sensitive REE emission lines in FAES and ICP AES and the DLs typically obtained by ICP AES are summarized in Table 43.3. Mutual spectral coincidences are serious. Flame AES offers DLs down

TABLE 43.3

Emission lines and detection characteristics for REE in FAES and ICP AES

Element	Wavelength (nm) (DL,ng/ml)		Element	Wavelength (nm) (DL,ng/ml)	
	FAES	ICP AES		FAES	ICP AES
Y	362.1	371.03 (2) 360.07 (3)	Gd	440.2	342.25 (14) 335.05 (10)
La	579.1	379.48 (10) 408.67 (2)	Tb	431.9	350.92 (10) 384.87 (40–50)
Ce	569.9	418.66 (50) 413.38 (50)	Dy	404.6	353.17 (5) 340.78 (10)
Pr	495.1	390.84 (20) 414.31 (30–50)	Ho	405.4	339.9 (3) 345.6 (10)
Nd	492.4	406.11 (10) 401.23 (10) 430.36 (30–55)	Er	400.8	349.91 (10) 236.06 (15–20)
Pm	—	—	Tm	371.8	346.33 (10) 313.13 (5) 384.80 (10)
Sm	476.0	359.26 (5) 442.43 (10)	Yb	398.8	28.94 (1) 369.42 (2)
Eu	459.4	381.97 (2) 412.97 (5–10)	Lu	451.9	261.54 (1) 307.76 (10)

to the sub-ppm levels for La, Ce, Pr and Nd using the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame [78]. Determination of REEs (except Ce) by FAES using a high resolution monochromator proved to be of value especially for Eu and Yb (DLs of 10–100 ng ml⁻¹) [79]. Gadolinium, Pr, Tb could be measured with a moderate sensitivity (DLs of 200–500 ng ml⁻¹) whereas the low-level determination of Ce and Lu was found to be impossible [79]. Trace analysis by ICP AES is hampered by inadequate DLs for some REEs, spectral interferences from the matrix (especially by Ca and easily ionizable alkali metals) and, further, by the mutual interferences among REE lines. Spectral interferences in AES have been exhaustively discussed [33,40,51], with particular emphasis on those from the matrix elements [80]. In particular, the determination of Tb is disturbed by Zr at the most sensitive wavelength; all the other lines are weak or interfered with by La, Ce and Nd; that of Tm and Er is

interfered with by Ni [81] and Ca [54], respectively. Spectral interferences are definitely avoided by HPLC separation prior to detection [40,59,61,82]. ICP AES of Y has been discussed [83]. Electrothermal vaporization ICP AES offered ADLs of 0.1–10 ng; a PTFE slurry was used to prevent the formation of refractory carbides [84]. When a W-coil ETV atomizer was used, ADLs for Er, La, Lu and Y were lower than those for GF AAS whereas for Eu, Sc, Tm and Yb they were comparable [85]. A much lower background emission and simpler spectra were claimed to be obtained with a newly developed microwave plasma torch [86]. The determinations of REEs by ETA AAS, FANES and furnace ionization non-thermal excitation spectrometry have been compared [87].

Thermal ionization mass spectrometry

Key data for the MS determination of REEs are summarized in Table 43.4. Monoisotopic REE (Y, Pr, Tb, Ho, Tm) are free from isobaric overlaps, whereas others have one (La, Ce, Lu), two (Sm, Eu, Gd, Dy, Er) or three (Nd, Yb) isotopes free from such an interference. Thermal ionization MS has been reviewed and possible mass overlaps have been discussed in detail [29]. Yttrium, Pr, Tb, Ho, Tm and Lu which are monoisotopic cannot be determined. Barium is the principal interferent and must be separated [29]. Suppression of isobaric interferences in the determination of REEs by direct loading TI ID MS down to 0.1 pg has been discussed [89]. Prior to TI MS, REEs were chromatographically separated into three fractions: (1) La and Ce; (2) light REEs (Gd, Eu, Sm, Nd); and (3) heavy REEs (Yb, Er, Dy) [29,57]. Thermal ionization MS of Nd isotopes has drawn particular attention [31,90,91]. The ratios $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ were corrected for mass fractionation by normalizing to $^{145}\text{Nd}/^{144}\text{Nd}$. ^{150}Nd enriched was the spike [31]. Simultaneous ID analysis of Nd and Sm with a fixed multicollector MS has been reported [92].

Inductively coupled plasma mass spectrometry

Inductively coupled plasma MS offers sufficiently low DLs (*cf.* Table 43.4) to enable a simultaneous determination of all the REE without their separation from the matrix using calibration with aqueous standard solutions [88]. Internal standard, e.g. In [10,93] or the Ru–Re pair [94], have been employed to correct for salt and acid suppression. Polyatomic ions are generally not present within the mass range of the REE in the HNO_3 blank spectra. The nuclides: ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb and ^{175}Lu are

TABLE 43.4

Selected data for the MS determination of the REE

Element	Stable isotopes (relative abundance)	Tracer in TI MS	Isotope ratios measured	ICP MS DL (ng/ml ^a)
Y	⁸⁹ Y (100)	—	—	0.10
La	¹³⁸ La (0.09); ¹³⁹ La (99.91)	138	¹³⁸ La/ ¹³⁹ La	0.075
Ce	¹³⁶ Ce(0.19); ¹³⁸ Ce(0.25); ¹⁴⁰ Ce(88.47); ¹⁴² Ce(11.08)	142		0.1
Pr	¹⁴¹ Pr(100)	—	—	0.09
Nd	¹⁴² Nd (27.16); ¹⁴³ Nd (12.18); ¹⁴⁴ Nd (23.83); ¹⁴⁵ Nd (8.3); ¹⁴⁶ Nd (17.17); ¹⁴⁸ Nd (5.74); ¹⁵⁰ Nd (5.62)	143	¹⁴³ Nd/ ¹⁴⁴ Nd, ¹⁴³ Nd/ ¹⁴⁶ Nd	0.2
Sm	¹⁴⁴ Sm (3.07); ¹⁴⁷ Sm (15.0); ¹⁴⁸ Sm (11.24); ¹⁴⁹ Sm (13.82); ¹⁵⁰ Sm (7.38); ¹⁵² Sm (26.73); ¹⁵⁴ Sm (22.75)	149	¹⁴⁹ Sm/ ¹⁴⁷ Sm	0.2
Eu	¹⁵¹ Eu (47.77); ¹⁵³ Eu (52.23)	153	¹⁵³ Eu/ ¹⁵¹ Eu	0.06
Gd	¹⁵² Gd (0.20); ¹⁵⁴ Gd (2.18); ¹⁵⁵ Gd (14.8); ¹⁵⁶ Gd (20.47); ¹⁵⁷ Gd (15.65); ¹⁵⁸ Gd (24.83); ¹⁶⁰ Gd (21.86)	155	¹⁵⁵ Gd/ ¹⁵⁶ Gd, ¹⁵⁵ Gd/ ¹⁵⁷ Gd	0.1
Tb	⁵⁹ Tb (100.0)	—	—	0.03
Dy	¹⁵⁶ Dy (0.06); ¹⁵⁸ Dy (0.10); ¹⁶⁰ Dy (2.34); ¹⁶¹ Dy (18.91); ¹⁶² Dy (25.51); ¹⁶³ Dy (24.9); ¹⁶⁴ Dy (28.19)	161	¹⁶¹ Dy/ ¹⁶² Dy ¹⁶¹ Dy/ ¹⁶³ Dy	0.1
Ho	¹⁶⁵ Ho (100)	—	—	0.04
Er	¹⁶² Er (0.13); ¹⁶⁴ Er (1.6); ¹⁶⁶ Er (33.61); ¹⁶⁷ Er (33.61); ¹⁶⁸ Er (26.79); ¹⁷⁰ Er (14.93)	167	¹⁶⁷ Er/ ¹⁶⁶ Er ¹⁶⁷ Er/ ¹⁶⁸ Er	0.06
Tm	¹⁶⁹ Tm (100)	—	—	0.01
Yb	¹⁶⁸ Yb (0.13); ¹⁷⁰ Yb (3.04); ¹⁷¹ Yb (14.28); ¹⁷² Yb (21.83); ¹⁷³ Yb (16.13); ¹⁷⁴ Yb (31.83)	171	¹⁷¹ Yb/ ¹⁷² Yb ¹⁷¹ Yb/ ¹⁷⁴ Yb	0.06
Lu	¹⁷⁵ Lu (97.42); ¹⁷⁶ Lu (2.58)	—	—	0.05

^a From Ref. [88]; — determination not possible.

free of isotopic overlaps in ICP MS [93]. The most common interferences are due to the formation of oxides from Ba and REE themselves. Reduction of polymeric, doubly charged and oxidic species by optimization of operating conditions has been comprehensively discussed [93, 95]. Yttrium, La, Ce, Pr, Nd and Sm could be determined directly in the mineral acid solutions without careful reference to the problem of oxide interferences [95]. Gadolinium could not be determined successfully at all while errors on Eu, Tb, Yb and Lu were high. Dysprosium, Ho, Er and Tm with only minor interferences from Sm and Eu show much smaller errors [95]. The monoisotopic Ho suffers from the overlap from $^{149}\text{Sm } ^{16}\text{O}^+$ at mass 165 which was alleviated by increasing the Ho^{2+} to Ho^+ ratio by appropriate instrumental settings and measuring Ho at the 82.5 mass [96]. Mathematical correction procedures for spectral overlaps with M^+ , MO^+ and MOH^+ ions have been comprehensively discussed [97,98]. The ultimate method to eliminate the interferences is the chromatographic separation prior to *on-line* ICP MS detection [60,62,99] which usually offers DLs of 1–5 pg ml^{-1} [60]. Electrothermal vaporization ICP MS from a W furnace offers DLs of 0.1–0.6 pg ml^{-1} [100] and a considerable freedom from the oxide interferences.

Neutron activation analysis

Neutron activation analysis is widely used because of the high neutron cross-section of most REEs. Basic analytical data for INAA of REE are summarized in Table 43.5. Dysprosium and Er have exclusively short-lived radionuclides and a separate short irradiation is required for their determination [35,52]. For Er, counting of the $^{167\text{m}}\text{Er}$ [101] can be used instead. The most common interference is the formation of some REE (La, Ce, Nd, Sm) from fission of uranium which cannot be alleviated by radiochemical separation [30,102–104]. Uranium must be separated prior to irradiation; otherwise mathematic correction needs to be employed. Instrumental analysis is further hampered by spectral interferences which include, for example, ^{24}Na for Pr and Er and ^{131}Ba for Eu and Yb. In the case of ^{153}Gd which is interfered with by ^{153}Sm , the Sm is allowed to decay before Gd is counted. Iron and Sc are separated radiochemically. Yttrium is usually not determined along with the lanthanides because it lacks suitable γ -peaks.

Fluorescence techniques

Dysprosium, Sm and Eu fluoresce when incorporated in an Na_2WO_4 matrix and exposed to UV radiation. Energy-dispersive XRF with an

TABLE 43.5

Basic neutron activation analysis data for the rare earth elements

Element	Radio-nuclide	Half-life	E γ (keV)	DL* (ng ml ⁻¹)
Y	⁹⁰ Y	64.2 h	β^+	
La	¹⁴⁰ La	1.7 d	329,487,816,1597	0.2
Ce	¹⁴¹ Ce	32.5 d	145	0.1
Pr	¹⁴² Pr	19.7 h	1576	0.1
Nd	¹⁴⁷ Nd	11.1 d	91,531	0.09
Sm	¹⁵³ Sm	46.8 h	103	0.003
Eu	^{152m} Eu	9.3 h	344	0.003
	¹⁵² Eu	12.1 y	344,1408	0.005
Gd	¹⁵³ Gd	242 d	103.2	
	¹⁵⁹ Gd	18 h		
Tb	¹⁶⁰ Tb	72.1 d	879	0.04
Dy	¹⁶⁵ Dy	2.33 h	280	0.02
Ho	¹⁶⁶ Ho	27.2 h	80.6	
Er	¹⁷¹ Er	7.52 h	308	0.03
Tm	¹⁷⁰ Tm	127 h	84.3	
Yb	¹⁶⁹ Yb	32.6 d	64,198	0.02
	¹⁷⁵ Yb	4.19 h	396	0.007
Lu	¹⁷⁷ Lu	6.71 d	208	0.002

* Values taken from Refs. [35,56].

isotope source has been widely used [46,48,58,105]. Iron, Ti and Mn interfere so a separation–preconcentration step is mandatory. Thin-film WD XRF [52] and TXRF [106,107] have been proposed alternatively. Laser-excited fluorescence in the ICP offered DLs below 1 $\mu\text{g ml}^{-1}$ without any interference from 100-fold excess of other REE except Sm, Pr and Ho [108]. Laser-induced time-resolved derivative fluorescence for Dy, Eu, Sm and Tb of their ternary complexes with TFA and TOPO has been reported [109].

43.3 ANALYSIS OF REAL SAMPLES

Water

The REEs are widely distributed in seawater in which they are present as carbonato complexes, e.g. $\text{La}(\text{CO}_3)^+$. Lanthanum, Ce, Nd occur at the 2–5 ppt level; other REE are 4–20 times less abundant. In natural waters REEs can be determined directly by ICP MS [110]. Other techniques involve a preconcentration step, usually by coprecipitation; INAA [30,102–104] and TI MS [29,31,111] are widely used. Analytical methods for the determination of REE in environmental waters are summarized in Table 43.6.

Rocks

Methods for the determination of REEs in geosamples have been reviewed [113]. Although direct methods such as slurry ICP MS [114] and LA ICP AES [115] have been reported, sample decomposition usually precedes the analysis. The REEs are generally concentrated in minor mineral phases (zircon, garnet) resistant to acid attack and PTFE bomb digestion is recommended [81,116]. Losses of heavy REEs in open beaker digestion with HF were reported [117]. Sintering with Na_2O_2 [81], fusion with LiBO_2 [39,117,118] or alkaline fusion [36,52,119] are alternatively used. Various decomposition procedures have been compared for sedimentary rocks [120]. The solution obtained can be analyzed directly by ICP MS (down to 0.1 ppm) [93,95,97,121–123] or less often by ICP AES [124–126] or TXRF [107]. A separation step generally improves accuracy; ion exchange is the most common. An additional coprecipitation step improves the low recoveries found for Sm, Eu and Gd for Fe- and Al-rich samples [33] and increases the number of lanthanides determined [119]. Removal of Fe(III) with HCl enables determination of Tm [119]. An automatic sample preparation for geosamples (weighing, fusion with LiBO_2 , dissolution, cation exchange separation) followed by ICP AES determination has been developed [127]. Several studies have compared the performance of different analytical techniques [116,128,129]. Matrix matching [120] and internal standardization with Tm or Y [124,130] are commonly used to compensate for the acid and salt depression effects in ICP AES. Analytical methods for the determination of REEs in rocks are summarized in Table 43.7. Speciation of the REE tetraphenylporphyrine complexes by reversed-phase chromatography with UV detection has been reported [132,133].

TABLE 43.6

Analytical methods for the determination of REE in natural waters

Water (amount)	Preconcentration	Detection	Element(s) determined (DL, ng/l)	Ref.
Sea (0.1–1 l)	extraction with a mixture of HDEHP and DHEHP (heptane); back-extraction (H ₂ O)	ICP MS	All (0.1–1) except for La (3) and Nd (2.5)	10
Sea (2–5 ml)	coprecipitation with Fe(OH) ₃ , extrn. of Yb from 8 M HCl into 2,6 dimethyl-4-heptanone	GF AAS	Yb (n.g)	27
Sea (1 l)	extraction with a crown ether carboxylic acid (CHCl ₃); back-extrn. (HNO ₃)	INAA	Eu, Lu (0.02 ^a); La, Sm (0.2–0.3 ^a)	23
Sea (10 l), pore	coprecipitation with Mg(OH) ₂ , copptn. with CaC ₂ O ₄	ICP AES	Ce, Y (<1)	5
Natural (1 l)	coprecipitation with Fe(OH) ₃ , cation exchange	ID MS	La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu (n.g)	29
Mineral	cation exchange	ICP AES	All (1–6) except Y, Yb, Lu (<1), Ce (10)	112
Hot spring, crater lake (0.2–3 l)	coprecipitation with Al(OH) ₃	INAA	lanthanides	30, 104
Water	evaporation with HCl	ETA AAS	La	71
Water	coprecipitation with Fe(OH) ₃ , cation exchange, anion exchange	TI MS	Nd isotopes	31

TABLE 43.7

Analytical methods for the determination of REE in rocks

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	Element(s) determined (DL, µg/g)	Ref.
0.8 g	HF-HClO ₄	cation exchange	ICP MS TI MS	All	129
0.15 g	HNO ₃ -HF	cation exchange	TI MS	La isotopes	57
(n.g.)	HF-HNO ₃ , (bomb); HNO ₃ - HClO ₄	cation exchange	ID MS	La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb	116
1 g	HF, HNO ₃ , HClO ₄ , HNO ₃ - HClO ₄	copptn. with CaC ₂ O ₄ ; cation exchange	ICP AES	All (n.g.)	33
1 g	(1) HClO ₄ -HF; (2) fusion with NaOH; dissoln. in HCl	matrix removal as SiF ₄ ; extrn. with HDEHP- DHEHP (heptane); back extrn. (HNO ₃)	ICP MS	All (0.1-1) ^a	11
0.25 g	fusion with Li ₂ B ₄ O ₇ , dissoln. HF-HNO ₃	anion exchange	ICP AES	All	39
0.25 g	evapn. with HF, HNO ₃ -HCl-HF (microwave assisted)	anion exchange, copptn. with rhodizonate and tannin	WD XRF	All excl. Y (<<1 µg)	39
0.3 g	HF-HNO ₃ - HClO ₄	cation exchange	ICP AES	Y, Yb, Lu (<1); La, Eu, Gd, Tb, Dy, Ho (1-10); Sm, Er, Nd, Pd, Ce (>10)	51
1 g	HF-HClO ₄	copptn. with CaC ₂ O ₄	ICP AES	All and Y (<0.1) except La, Ce, Pr, Nd, Sm, Tb, Er (<1)	34

continued

TABLE 43.7 (continuation)

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	Element(s) determined (DL, µg/g)	Ref.
1 g	HCl-HNO ₃ - HF-HClO ₄	ion exchange	ICP AES	All excl. Y (n.g.)	131
1 g	HF-HNO ₃ , HNO ₃ -H ₂ O ₂	copptn. with CaF ₂	GF AAS ICP AES	Ce, Pr, Nd, Tb, Ho, Er, Tm, Lu, Y, La, Ce, Sm, Eu, Gd, Dy, Yb	37
1 g	HF-HNO ₃	extrn. of Fe as FeCl ₄ ⁻ (MIBK); AE, copptn. as rhodizonate	WD XRF ED XRF	lanthanides (1 ^b)	38
1-2 g	evapn. with HF, HNO ₃ , HClO ₄ , HNO ₃ -H ₂ O ₂	cation exchange	ETA AAS	lanthanides	49
n.g.	fusion with Na ₂ O ₂ -NaOH	ion exchange	ICP AES	lanthanides (n.g.)	52
n.g.	fusion with Na ₂ O ₂ -NaOH	ion exchange; copptn. with Fe(OH) ₃	WD XRF	lanthanides (n.g.)	52
n.g.	HF-H ₂ SO ₄ , the residue fused with Na ₂ CO ₃ - Li ₂ B ₄ O ₇	extrn. with TOPO (MIBK)	ICP AES	All (<1) except for Yb, Lu, Y, Dy, Ho (<0.1)	118
n.g.	n.g.	cation exchange	RNAA	All except Pr	53
0.5 g	HNO ₃ -HClO ₄ - HF	cation exchange HPLC	ICP AES	Y, Ce, Nd, Eu, La, Y, Sm, Dy, Yb, Gd	82
1 g	sintering with Na ₂ O ₂ , dissoln. in HCl	cation exchange	ICP AES	All except Tm, Tb	81
1 g	HF-HNO ₃ , evapn., dissoln. in HCl	cation exchange	ICP AES	La, Ce, Nd, Sm, Eu, Gd, Dy, Yb, Lu (n.g.)	52

Sample (amount)	Decomposition	Separation and/or pre-concentration	Detection	Element(s) determined (DL, µg/g)	Ref.
1 g	fusion with KF_2 , dissoln. in HF – HCl , HClO_4	cation exchange	GF AAS	lanthanides except La, Ce (n.g)	50
1–3 g	fusion with Na_2CO_3	copptn. with $\text{Al}(\text{OH})_3$	RNAA	lanthanides except Pr, Er	119
0.1 g	n.g.	CE or copptn. with CaC_2O_4 or $\text{Fe}(\text{OH})_3$	ETA AAS	Y, Nd, Sm (few), Eu, Dy, Ho, Er, Tm, Yb (<1)	77
0.05 g	fusion with Na_2O_2 – NaOH	copptn. as fluorides	RNAA	La, Ce, Pr, Nd, Sm, Eu, Gd	36

^a In the sample, pg/g; ^b absolute detection limit, µg

Biological samples

The increased release of REEs into the environment is prompting monitoring studies in the relevant matrices. Biological materials have been analyzed after dry ashing for individual REE by a number of techniques [5,71]. For multielement analysis wet digestion is preferred [134]. Combined procedures for biological and environmental materials are summarized in Table 43.8.

TABLE 43.8

Determination of rare earth elements in biological and environmental materials

Sample (amount)	Decomposition	Separation and/or pre-concentration	Detection	Element(s) determined (DL)	Ref.
Plasma, human tissue	HNO_3 – HCl	cation exchange	RNAA	La, Ce, Nd, Eu, Yb	56
Biotissue (1g) biofluid (1 ml)	HNO_3	extrn. with 4-benzoyl-3-methyl-1-phenyl-2-pyrazoli n-5-one (MIBK)	ETA AAS	Gd (2 ng)	70

continued

TABLE 43.8 (continuation)

Sample (amount)	Decomposition	Separation and/or pre- concentration	Detection	Element(s) determined (DL)	Ref.
Algae (1 g)	HNO ₃ (bomb)	copptn. with CaC ₂ O ₄	RNAA	La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Er, Yb, Lu	35
Plant (0.2 kg)	dry ashing	anion exchange	ED XRF	La (0.09), Ce(0.03), Nd (0.05) ppm	58
Plant CRMs (0.1 g)	H ₂ SO ₄ -H ₂ O ₂	copptn. with Mg(OH) ₂ copptn. with CaC ₂ O ₄	INAA	Eu, Lu (0.02 ng) La, Sm (0.2-0.3)	23
Soil (10 g), dust (2.5 g)	HNO ₃	matrix removal as SiF ₄ ; anion exchange	ED XRF	La (17), Ce (6); Nd (16) ppm	58
Sediment (0.2 g); biota (0.2 g)	HF-HClO ₄ - HNO ₃ (bomb); HF-HClO ₄	cation and anion exchange	TIMS	Nd isotopes	31
Sediment CRM (1 g)	HNO ₃ -HF	cation exchange	ICP AES	Eu, Yb, Lu (0.01); La, Gd, Dy (0.1) ; Ce, Nd, Sm (0.2) ppm	55
Fly ash (1 g)	HF-HNO ₃	cation exchange	ICP AES	La, Ce, Nd, Sm, Eu, Gd, Dy, Yb, Lu (n.g.)	52
Fly ash (0.1 g)	HNO ₃ -HF- HClO ₄ (bomb)	cation exchange, HPLC	ICP MS	All (<2 ng/ml) except La (5 ng/ml)	62
Environ- mental CRMs (5-10 g)	HF-HClO ₄ (bomb), evapn., dissoln. in HCl	cation exchange	ETA AAS ICP AES	Er	54

TABLE 43.9

Determination of rare earth elements in industrial materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection technique	Element(s) determined (DL, $\mu\text{g/g}$)	Ref.
Gd matrix		cation exchange chromatography	ICP MS	Tm, Yb, Lu (<1)	60
U-oxides (10 g)	HCl (UO_3) HCl- HNO_3 (UO_2)	extraction of U with Alamine 336 (<i>o</i> -xylene-petroleum ether)	DCP AES	Sm, Eu, Gd (<1)	138
Uranium (0.02 g)		removal of U by RPC; cation exchange	VIS	Sm, Gd, Eu, Dy (0.02)	139
Lanthanum		cation exchange chromatography	ID ICP MS	Nd (0.01 ng/g)	140
Uranium (10 g)	HNO_3	sorption on cellulose filled with Et_2O and HNO_3	ICP AES	Gd, Eu (0.04); Dy, Sm, Ce (0.1)	41

Industrial samples

In many products REE are present at the per cent levels which are readily accessible by ICP AES. REE in bauxites [128], steel [135], glass fibres [136] and nuclear grade graphite [130] have been determined by ICP or DCP AES after sample decomposition. Determination of REE in Y, La, Gd and Yb metals using high resolution ICP AES has been developed [137]. Separation from the matrix is necessary. Combined analytical procedures are summarized in Table 43.9.

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Rhenium

Rhenium (Re, atomic weight 186.21, melting point 3180°C, $d = 21.0 \text{ g cm}^{-3}$) is a silvery-grey metal. It occurs in the earth's crust with an average abundance of 0.7 ppb, primarily concentrated in molybdenites associated with copper. The metal dissolves in HNO_3 , concentrated H_2SO_4 and H_2O_2 to produce the perrhenic acid (HReO_4). It occurs in various oxidation states but the Re(VII) compounds are the most stable. In solution, Re occurs almost entirely as ReO_4^- for a wide range of acidities. Rhenium is highly refractory and corrosion resistant but its applications are restricted owing to its scarcity and high cost. The β -emission decay scheme, $^{187}\text{Re} \rightarrow ^{187}\text{Os}$ ($t_{1/2} = 1.52 \times 10^{11}$ years) offers a convenient opportunity to study the age of ore deposits and extraterrestrial samples.

44.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

The major interference in the determination of Re is usually due to Mo which occurs at large excess in most analyzed samples. Extraction of ion pairs of ReO_4^- with TBA [1], TPP [2] or TPA [3] is widely used; low Re recoveries occur in 2–4 M H_2SO_4 (the medium usually left after osmium distillation) [4]. Perrhenate is efficiently retained by anion exchangers from H_2SO_4 (<2.5 M), HCl (<5 M), and HNO_3 (<1 M) and can be eluted with 3–8 M HNO_3 [3–8]. Perrhenate passes through cation exchangers from a slightly acidic solution while many metals (Na, Mg, Al, K and Ca) are retained [9]. Rhenium heptoxide can be volatilized from HClO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ – H_2SO_4 media at a temperature above 250°C. Osmium is usually distilled off as OsO_4 beforehand.

Molybdenum is partly codistilled. Rhenium can be separated from many metals by precipitation as ReS_2 with As(III) as collector or as an insoluble salt of ReO_4^- with an organic counter-ion, e.g. TPA [10].

Spectrophotometry

Spectrophotometric determination of Re based on ion pairs of ReO_4^- with basic dyes is sensitive ($\epsilon = 1.0\text{--}1.2 \times 10^5$) but requires the separation of Re beforehand because of poor selectivity [11,12]. Extraction-spectrophotometric method based on the reaction of Re with α -furildioxime in acid medium containing SnCl_2 ($\epsilon = 4.1 \times 10^4$ at 530 nm) is an alternative. Oxidants, Mo, Pd, Cu, SCN^- , NO_3^- and F^- interfere and must be removed prior to determination.

Atomic absorption spectrometry

Because to the refractory character of Re high atomization temperatures are required and the sensitivity obtained is rather poor. Flame AAS gives a sensitivity of *ca* $10 \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O-C}_2\text{H}_2$ (reducing, rich) flame at the most sensitive 346.0 nm line. Large excesses of Al, Ca, Fe, Pb, Mn, Mo and U interfere; matrix matching is necessary. Graphite furnace AAS has no practical significance; its sensitivity for Re (ADL *ca* 0.5 ng) is one of the poorest achieved because of the formation of thermally stable carbides [3,13].

Inductively coupled plasma atomic emission spectrometry

The high temperature of the ICP ensures *ca* 93% ionization of Re [14] which results in a 1000-fold increase in sensitivity compared with AAS. The most sensitive line: 227.525 nm (DL 12 ng ml^{-1}), is interfered with by Ca [13] while the others: 346.047 nm (DL 25 ng ml^{-1}) and 346.472 nm (DL 40 ng ml^{-1}) are interfered with by Mo and Mn, respectively. The practical significance of ICP AES is restricted to concentrates and metallurgical samples. The sensitivity (and selectivity) may be increased by the introduction of Re as Re_2O_7 vapour into the plasma.

Mass spectrometry

Rhenium has two naturally occurring isotopes ^{185}Re and ^{187}Re with relative abundances of 37.4% and 62.6%, respectively. Isotope dilution TI MS [7] and RI MS [15,16] determination has been discussed. Possible isobaric interferences include BaO_3 , EuO_2 and TmO at the mass of 185 and LaO_3 , GdO_2 and YbO at the mass of 187. In molybdenum concentrates there is a possibility of MO_2^+ interference at 187, which can be,

however, eliminated by comparison of ^{185}Re and ^{187}Re intensities with the natural abundances. The isobaric interference from ^{187}Os is corrected by determination of Os intensity at mass 189. ICP MS is particularly advantageous because of high sensitivity due the high ionization efficiency of Re [8,17,18]. An ADL of 10 fg has been reported [6]. Molecular oxide interferences are negligible with laser sampling [19].

Neutron activation analysis

Either ^{186}Re ($t_{1/2} = 90.6$ h, $E_\gamma = 0.137$ MeV) or ^{188}Re ($t_{1/2} = 17$ h, $E_\gamma = 0.15$ MeV and others) can be measured. A chemical separation of rhenium is required because of the many interferences possible as a result of the low γ -ray energy [20].

44.2 ANALYSIS OF REAL SAMPLES

Methods for the determination of Re are summarized in Table 44.1. Perrhenate is the only significant Re species present in surface waters [3,9,23]. The reported concentrations of Re in marine waters (5–15 ng l⁻¹) [3] are significantly higher than those of Pt group metals. Determination of Re is usually preceded by anion-exchange preconcentration. *On-line* ICP MS systems for ground water analysis with *on-line* cation-exchange matrix separation [9] and for sediment pore and river waters with anion-exchange preconcentration [8] have been developed. Rhenium typically occurs at low ppt to low ppb levels in most common rocks. The volatility of Re in oxidizing solutions makes it difficult to remove the complex carbonaceous material without significant losses. Peroxide fusion has been recommended for carbonaceous chondrites [20]. Losses of Re(VII) are encountered during evaporation of solutions containing HF, HClO₄ and H₂SO₄. Phosphoric acid strongly suppresses the volatilization of Re(VII) from *aqua regia* and HF solutions [24]. Closed vessel decomposition or the use of a reflux is recommended. Anion-exchange resin and Ta filament material were found to be the major contributors to the Re blank [1,5]. Direct methods (GD MS and XRF) are preferred for the determination of Re in alumina based catalysts [25]. The determination of Re in oil refining catalysts by ID ICP MS has been discussed [26].

TABLE 44.1

Determination of rhenium in geological materials

Material (amount)	Sample decomposition	Separation	Detection technique	DL (ng/g)	Ref.
Rocks (0.5–10 g)	EtOH–HCl– HF (bomb)	extrn. with tribenzyl- amine (CHCl_3)	ID RI MS	few	1
Rock (0.15–0.5 g)	fusion with Na_2O_2 –NaOH	anion exchange, elution with 4 M HNO_3	ID TIMS	n.g.	7
Rocks	fusion with KOH	pptn. with TPA	NAA	10	10
Rocks	fusion with KOH, leaching with acetone	extrn. chromatogr. on a TBP–KEL(F) column	RNAA	10	21
Rocks	fusion with KOH	pptn. with TPA, distillation as Re_2O_7 , purification by extrn. chromatogr.	RNAA	1	22
Rocks, sediments (0.5 g)	fusion with Na_2O_2	anion exchange, extrn. with TPA	GF AAS	0.5 ^a	3
Sediments (0.5–1 g)	HF– HNO_3 (microwave assisted)	anion exchange as ReO_4^- , elution with 8 M HNO_3	ID ICP MS	0.005	8
Ores, con- centrates	fusion with Na_2O_2 – Na_2CO_3	leaching with acetone from 5 M NaOH	ICP AES	100	13
Ores	HNO_3 – H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, microwave assisted	anion exchange, elution with 12 M HNO_3	ID ICP MS	n.g.	18
Chondrites, meteorites	alkaline fusion	anion exchange	ID RIMS	n.g.	15
Chondrites (0.05–0.5 g), meteorite (0.2–0.4 g)	fusion with Na_2O_2	anion exchange	ID RIMS	few	5
Meteorites (1 g)	HNO_3 –HCl under reflux	distillation from H_2SO_4 containing CrO_3 , trapping in NaOH	NAA	n.g.	20

Material (amount)	Sample decomposition	Separation	Detection technique	DL (ng/g)	Ref.
Meteorites (0.1–0.2 g)	<i>aqua regia</i>	anion exchange, <i>on-line</i> oxidn. to Re_2O_7 with HClO_4	ICP MS	0.01 ^a	6

^a Absolute detection limit, ng.

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Rhodium

Rhodium (Rh, atomic weight 102.91, melting point 1970°C, $d = 12.4 \text{ g cm}^{-3}$) is a silvery-white, noble metal (one of the Pt group elements). It occurs in the earth's crust with an average abundance of 1 ppb, usually along with Pt ores. The metal dissolves in hot H_2SO_4 , hot HBr , in fused alkali metal bisulphates and in oxidizing fluxes. It occurs in the II, III, IV and VI oxidation states, the III one being the most common. In acidic media (H_2SO_4 , HClO_4 , dilute HCl) Rh is present as Rh^{3+} . Freshly precipitated Rh(III) hydroxide is soluble in excess alkali. Rhodium(III) forms a large number of complexes with halides, cyanide and ammonia. Rhodium is precipitated as metal by Zn, Mg and Fe; the yield increases in the presence of Pt or Pd. Trace analysis for Rh is usually demanded in geology and mining industry. The analytical chemistry of Rh has been reviewed [1–4].

45.1 SEPARATION AND PRECONCENTRATION

Chemical reactions of Rh are affected by incomplete conversion and unknown speciation in the solution. While evaporating solutions of Rh overheating of the residues should be avoided as compounds insoluble in water and acids may be formed. In weakly acidic solutions polymeric rhodium forms may not be converted into an analytically determinable form.

Ion exchange

Rhodium(III) is retained on cation exchangers from dilute HCl medium and is thus separated from Ir, Pt and Pd. The retained Rh is difficult to desorb; the resin must often be ashed or decomposed by acid attack. An alternative approach is based on the formation of the anionic

chloro complex which is not retained on cationites. The RhCl_6^{3-} is only weakly retained by strongly basic anion exchangers and is typically eluted before other Pt group metals [3,5]. Alternatively, Rh(III) in HCl medium is passed through anionite while other Pt group metals are retained. Sorption of Rh on chelating resins [6,7] and polyurethane foams [8,9] has been reported. The Rh-bis(carboxymethyl)dithiocarbamate complex can be retained from an HCl-SnCl₂ medium on inert support [10]. Rhodium complexes with PAN [11] or 8-hydroxyquinoline have been separated by reversed-phase HPLC [12].

Coprecipitation

Zinc, Mg, Sb or other reductants, e.g. SnCl₂ [13–15], reduce Rh(III) to the metal. Tellurium [13,16–18], Hg [19] and Se [14,15] are suitable collectors. Rhodium may be separated from Ir(IV) by reduction to the metal with Sb powder in hot H₂SO₄, with Cu powder in HCl or as a compound with thioacetanilide and formamidinesulphinic acid. Coprecipitation of Rh with Al, Fe and Bi phosphates followed by the dissolution in HCl and separation from the carriers by precipitation with MBT [20] has been reported.

45.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometry is usually based on the coloured $\text{Rh}(\text{SnX}_3)_6^{3-}$ complexes (X denotes halogenide), formed *via* reaction of Rh with Sn(II) halides in HCl medium. The Pt group metals interfere and must be separated beforehand. The $\text{Rh}(\text{SnCl}_3)_6^{3-}$ reacts with basic dyes to form sparingly soluble compounds that are used for very sensitive flotation determination of Rh ($\epsilon = 4 \times 10^5$ at 530 nm) [21]. Numerous azo reagents have been proposed but the selectivity is poor. Catalytic methods have been reviewed [22].

Atomic absorption spectrometry

Flame AAS offers a sensitivity of 0.1–0.2 $\mu\text{g ml}^{-1}$ in the recommended air-C₂H₂ (very lean, oxidizing) flame at the most sensitive 343.5 nm line. The use of an N₂O-C₂H₂ flame improves linearity but sensitivity is degraded by a factor of 5. The determination is interfered with by many elements, especially Pt, Cu and P. The addition of 1% Na₂SO₄ is recommended to control chemical interferences and to improve linearity and sensitivity. Interference from Pt can be alleviated by CuSO₄ or ZnSO₄ [23]. Buffering with La₂(SO₄)₃ was found to be more effective for

the elimination of interferences from other metals and phosphorus [24]. Several organic solvents have been tested for FAAS determination of Rh, ethanol was preferred to MIBK [25]. Graphite furnace AAS offers a characteristic mass of *ca* 10 pg. Instrumental conditions have been extensively discussed and the importance of the nature of the graphite tube was stressed [5]. The enhancement effect of NiCl_2 and CoCl_2 on the Rh signal was observed using both pyrolytic graphite coated and uncoated tubes [5].

Other techniques

ICP AES offers a DL of $6 \mu\text{g ml}^{-1}$ at the most sensitive 343.5 nm line. In DCP AES the interference from many metals is alleviated by the use of an La–Li buffer [26]. Rhodium has only one stable isotope (^{103}Rh) and thus is not amenable to TI MS. A DL of 1 ng g^{-1} for the ICP-MS determination of Rh in ores was reported in a review paper [27]. The use of ETV with Ni as a matrix modifier resulted in 10-fold increase in sensitivity [28]. Prior to TXRF determination Rh must be separated from the matrix (e.g. by coprecipitation with Se) and the selenium needs further to be separated [14]. Neutron activation analysis is based on the reaction $^{103}\text{Rh}(n,\gamma)^{104\text{m}}\text{Rh}$ and counting the ^{104}Rh ($t_{1/2} = 42 \text{ s}$, $E_\gamma = 0.55 \text{ MeV}$) formed by the decay of the $^{104\text{m}}\text{Rh}$ ($t_{1/2} = 4.4 \text{ min}$) [29]. The typical interference is with As and Sb which should be removed prior to irradiation.

45.3 ANALYSIS OF REAL SAMPLES

Geological matrices

Lead fire assay allows for quantitative collection of Rh. Cupellation should be avoided since Rh may be partly oxidized and lost as a volatile oxide. The lead button contains Rh in the form of intermetallic compounds or very fine dispersions, and can be dissolved in a mixture of HCl and HNO_3 or HClO_4 [30]. Other collectors (alternative to or complementing lead) include Pt, Sn, Cu and Au, the last two being particularly suitable for Cu-rich ores. NiS fire assay also allows quantitative recovery of Rh [31–33]. Rhodium is a relatively soft metal and may adhere to the walls of the rings used for the pulverization of the NiS button [23]. Leaching with *aqua regia* is generally insufficient for quantitative recovery of Rh even if the matrix is degraded with HF beforehand. The insoluble residue should be fused with an oxidizing agent [15,17]. Recent methods for the determination of Rh in geological samples are summarized in Table 45.1.

TABLE 45.1

Determination of rhodium in geological materials

Material (amount)	Sample decomposition	Separation	Detection technique	DL, (ppb) ^a	Ref.
Rock (15 g)	lead fire assay	cupellation in a Au bead	GF AAS	0.1	34
Marine sediments	dissoln. HF- HCl-HNO ₃	copptn. with Al, Fe and Bi phos- phates, dissoln. in HCl, pptn. with MBT	ICP MS	n.g.	20
Rock, ore (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	RNAA	2	16
Sand, ore, rock (25 g)	NiS fire assay	none	INAA	2	35
CRMs (10 g)	NiS fire assay, the bead dissolved in HCl	none	GF AAS	n.g.	33
CRMs (20–30 g)	NiS fire assay, the bead dissolved in HCl	none	ICP-MS	0.1	31
Ore (50–100 g)	NiS fire assay, the bead dissolved in HCl	none	ICP AES GF AAS NAA	50 ^b 2 ^b 1	32
Chromite concentrates (3 g)	NiS fire assay or fusion with Na ₂ O ₂	copptn. with Te	FAAS	n.g.	18
CRMs (0.5 g)	HCl-HNO ₃	copptn. with Hg	GF AAS	n.g.	19
Sulphide ore	<i>aqua regia</i>	anion exchange	GF AAS	56 ^d	5
Rocks	HF- <i>aqua regia</i>	copptn. with Te	ETA AAS	1–2	13
Nodules (0.25 g)	HF- <i>aqua regia</i>	copptn. with Se	GF AAS	1 ^b	14
Rocks (5 g)	HF- <i>aqua regia</i> (bomb)	anion exchange	ETA AAS	1	36
Rock (0.5–1.5 g)	HNO ₃ -HF (bomb), H ₃ BO ₃	copptn. with Se	GF AAS	1 ^b	14
Rocks (5 g)	roasting, HF- H ₂ SO ₄ , fusion with Na ₂ O ₂ -NaKCO ₃	copptn. with Se	GF AAS	0.5	15

Material (amount)	Sample decomposition	Separation	Detection technique	DL, (ppb) ^a	Ref.
Rock, ore (2–5 g)	HF– <i>aqua regia</i> , the residue fused with Na ₂ O ₂	copptn. with Te	GF AAS	40 ^d	17
Rocks (0.5 g)	fusion with LiBO ₂	sorption on polyDDTC resin	ICP AES	100–200 ^b	37

^a Given in ppb in the sample unless stated otherwise; ^b in ppb in solution; ^d sensitivity.

Industrial materials

Fusion attack with Na₂O₂ [18] is almost always required for concentrates and mattes. Flame AAS and ICP AES are the usual determination techniques used. The same treatment applies to sweeps and alloys. Catalysts can be treated in a way similar to that described for Pt. Direct methods (e.g. XRF, GD MS) are preferred [38]. Rhodium has been determined in high purity platinum matrix, after pressure dissolution in *aqua regia* and extraction separation, by GF AAS [23].

Other samples

The results for Rh content in water and biological samples are at the detection limit (0.5 pg ml⁻¹ for water and 0.35 ng g⁻¹ for biotissues) [14]. Preparation and certification of a rhodium SRM solution (NIST 3144) has been described [39]. A concentration of 40–100 pg l⁻¹ of Rh was found in ocean waters by GF AAS and ICP MS after coprecipitation (from a 25-ml sample) with Al, Fe and Bi phosphates followed by dissolution in HCl and separation from the carriers by precipitation with MBT [20].

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Rubidium

Rubidium (Rb, atomic weight 85.47, melting point 39°C, $d = 1.53 \text{ g cm}^{-3}$) is a soft, silvery highly reactive alkali metal. It is widely abundant (0.003%) in the earth's crust and occurs together with Cs in certain potassium-bearing minerals. Rubidium is readily oxidized by air, forming a mixture of hydroxide and carbonate, and reacts vigorously with water and ethanol to evolve H_2 . In aqueous solutions Rb occurs as a monovalent cation, with no redox properties and only a weak tendency to form complexes with a restricted number of ligands, e.g. crown ethers. Rubidium determination is essential in geochronology, for the Rb–Sr isochrone dating.

46.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

The extraction of Rb with dicyclohexano-18-crown-6 and picrate as a counter-anion into CH_2Cl_2 is quantitative at pH 3–7. Rubidium may be stripped with 2M HNO_3 . Most alkali and alkaline earth metal ions do not interfere, but potassium is co-extracted to a large degree [1]. Extraction of Rb from alkaline solution with tetraphenylboron (Ph_4B^-) into DIBK proved to be reliable whereas in acidic media polyvalent cations may affect the recovery [2]. Cation-exchange separation of Rb has been reported but it generally lacks selectivity *vs* other alkali metal ions [3].

Atomic absorption spectrometry

No HCL is available for Rb; vapour discharge or EDLs are used. A red cut-off filter (below 650 nm) should be used to reduce the background. Flame AAS offers a DL of 2 ng ml^{-1} in the recommended

air-C₂H₂ (oxidizing, lean, blue) flame at the 780.0 nm line [4]. The addition of a K salt as an ionization buffer is recommended [4–7]. Aluminium and strong mineral acids reduce the Rb signal; matrix matching is important. Graphite furnace AAS offers a DL of 0.05 ng ml⁻¹ using platform atomization [4]. A DL of 2 ng ml⁻¹ was reached with a tungsten coil atomizer [8].

Atomic emission spectrometry

Flame AES offers a DL of *ca* 0.3 µg ml⁻¹ in a air-C₂H₂ flame at 780.02 nm [4,9]. Potassium interferes and matrix matching or standard additions calibration has to be used [2]. The fuel-rich H₂-air flame shows virtual freedom from inter-alkali-metal interferences at the expense of sensitivity. Potassium or Cs should be added as ionization buffers [9,10]. Phosphorus interferes [10]. The DLs obtained in ICP AES are much poorer (0.5 µg ml⁻¹ at 780.02 nm) and this technique is restricted to the determination of Rb in a multielement array (*cf.* Part II).

Mass spectrometry

Rubidium has two natural stable isotopes: ⁸⁵Rb (72.2%) and ⁸⁷Rb (27.8%). The determination by TI MS suffers from the inability to correct for fractionation and from difficulties in a clean separation of Rb from other alkali metals. In ICP MS the ⁸⁵Rb peak is preferably counted as the ⁸⁷Rb is interfered with by ⁸⁷Sr [11–13]. Application of ID ICP MS has been reported [3].

Neutron activation analysis

During irradiation a long-lived ⁸⁶Rb (*t*_{1/2} = 18.6 d, *E*_γ = 1.08 MeV) and short-lived ⁸⁸Rb (*t*_{1/2} = 17.8 min, *E*_γ = 1.85 and 0.91 MeV) are formed. As Rb is usually accompanied by large amounts of Na and K, radiochemical separation is necessary and the long-lived isotope must be used. Instrumental NAA was widely used in a multielement array for a variety of samples with a DL of *ca* 0.5 ppm [14–19].

Other determination techniques

No reliable spectrophotometric method can be found in the literature. Laser-induced atomic ionization in flames has been used for direct determination of Rb in various samples [20,21]. Atomic fluorescence spectrometry with laser excitation allowed a DL of 0.2 ng ml⁻¹ to be achieved [22]. Use of ED XRF with a ¹⁰⁹Cd source and a Si(Li) detector has been reported [23].

46.2 ANALYSIS OF REAL SAMPLES

Environmental materials

Rubidium can be determined in natural or mineral waters directly, after dilution with the ionization buffer by FAAS [6] or GF AAS [4]. The concentrations in fly ash can be measured by INAA [19] or ICP AES [24], usually as part of a multielement analysis.

Geological materials

Rubidium can be determined directly or on sample dissolution by GF AAS [7] and laser-induced atomic ionization in flames [21]. Lithium hydroxide is a suitable flux for basic and ultrabasic rocks as the bulk of the rock matrix (except some Al and Cr) is left behind whereas Rb and other alkali metals pass into solution [2]. Rubidium can be determined on extraction separation by FAES [1,2] and FAAS [1]. Dissolution of the barite samples by refluxing with an ammoniacal EDTA followed by dissolution of the residue with $\text{HF-H}_2\text{SO}_4$ has been proposed for GF AAS [25].

Biological materials

Rubidium in plasma or serum has roused only modest clinical interest. The technique most commonly used for analytical measurements is INAA [14,15], but FAES [9], GF AAS [26], ED XRF [23] and ICP MS [13] have been applied as well. Sensitivity of ICP AES and FAAS was found to be insufficient for Rb determination in blood [9]. Natural levels of Rb in insects can be determined by GF AAS [5]. Foodstuffs have been analyzed by INAA [17] and flame AES [10].

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Ruthenium

Ruthenium (Ru, atomic weight 101.07, melting point 2310°C, $d = 12.4 \text{ g cm}^{-3}$) is a white noble metal, one of the Pt group elements. It occurs in the earth's crust with an average abundance of 1 ppb, along with the other Pt group metals, in Cu and Ni sulphide ores or as a minor component in osmiridium. Finely divided Ru dissolves in alkaline hypochlorite solutions. It is also dissolved by fused alkali containing an oxidizing agent, with formation of perruthenate (RuO_4^-) and ruthenate (RuO_4^{2-}). The most common oxidation states are III, IV, VI and VIII. Ruthenium(III) can be reduced in weak acid solutions by Zn, Mg or Fe to the metal. The recovery is seldom quantitative but increases if an excess of Pt and/or Pd is coprecipitated. Powerful oxidants convert Ru in the compounds into the volatile (boiling point 108°C) tetroxide, RuO_4 . It dissolves in alkalis with the formation of the green perruthenate, RuO_4^- , at the beginning, and then an orange solution of ruthenate. Halide complexes of Ru(IV) are less stable than similar complexes of Os(IV). Different aspects of analytical chemistry of Ru have been reviewed [1–4]. The need for trace analysis for Ru is practically restricted to geology.

47.1 SEPARATION AND PRECONCENTRATION

Speciation of Ru in aqueous solutions is extremely complex and dependent on many variables. The lack of knowledge about the forms actually present and kinetics of the reaction makes handling Ru solutions very tricky and to be avoided whenever possible.

Volatilization

Volatilization of RuO_4 from H_2SO_4 or H_3PO_4 containing an oxidant (e.g. KMnO_4 , NaBiO_3 , HClO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) is the most popular. The distilled RuO_4 is absorbed either in acid solutions containing reductants or in alkaline solutions. Only OsO_4 and to some extent Re_2O_7 can codistil. Osmium is separated by a preliminary distillation from boiling H_2SO_4 containing H_2O_2 (cf. Chapter 40). The volatilization behaviour of Ru has been discussed [5,6].

Extraction

Extraction of RuO_4 into inert solvents (CCl_4 , CHCl_3 , C_6H_6) from dilute H_2SO_4 or HNO_3 is popular [7,8]. Ruthenium may be stripped from the organic phase with a solution of sulphite or KOH. The chloride and bromide complexes of Ru(III) can be extracted from HCl and HBr solutions by amines and oxygen-containing organic solvents. Ruthenium can be separated from Os by extraction as a compound with diphenylthiourea, or as the ion pair of RuO_4^{2-} with TPA.

Other methods

Ruthenium was coprecipitated with Te [9,10] or with Pt group metals on reduction with formic acid [11]. Adsorption of microamounts of Ru on hydrous iron oxides has been reported [12]. Ruthenium was retained on chelating resins [13] or polyurethane foam as $\text{Ru}(\text{SCN})_6^{3-}$ [14]. Reversed-phase LC separation of Ru as 8-hydroxyquinolate [15] or di-ethyl-dithiocarbamate [16] from other Pt metals has been discussed.

47.2 DETERMINATION TECHNIQUES

Spectrophotometry

The most common method is based on the reaction of Ru in strong acid media with 1,4-diphenylthiosemicarbazide in the presence of SnCl_2 to produce a red-violet ($\epsilon = 1 \times 10^4$ at 560 nm) complex extractable into CHCl_3 . A 10-fold excess of Os does not interfere but Re interferes in any amount. Ruthenium can be determined in the presence of Os as the chloride complex by second-order derivative spectrophotometry [17]. Flotation of the ion associate of the chloro complex of Ru with Rhodamine 6G is the basis of a very sensitive method ($\epsilon = 5.1 \times 10^5$) [18]. A chemiluminescence method based on the catalytic effect of Ru(III) on the oxidation of proflavine-*N,N,N',N'*-tetraacetic acid by H_2O_2 was reported to offer a DL of 1 ng ml^{-1} [19].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.5\text{--}1\ \mu\text{g ml}^{-1}$ in the recommended air-C₂H₂ oxidizing flame at the most sensitive 349.9 nm line. The addition of U(VI), CuSO₄ or KCN improves the atomization efficiency of Ru(III) [20]. The absorption is suppressed by base elements, Mo, Pt and H₃PO₄ [21]. The interference is alleviated by buffering with La₂(SO₄)₃ or KHSO₄ [21]. Lanthanum and Sr were shown to be advantageous over Na and K as ionization suppressors [22]. The effect of MIBK and EtOH was studied; that of the latter was found to be more advantageous [23]. The sensitivity is increased 60-fold in the presence of strong oxidants, e.g. Ce(IV), owing to the improved transport and atomization efficiency of the RuO₄ formed [20].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 30 pg. Graphite tubes coated with a layer of tantalum carbide are recommended to avoid serious interferences from many metals. Carbidization of the graphite tubes also increases the maximum permissible charring temperature of Ru from 1500 to 2400°C without any loss of the element [24]. Iridium at more than 50-fold excess interferes [25].

Neutron activation

Neutron activation of Ru yields ¹⁰³Ru ($t_{1/2} = 39.8\text{ d}$, $E_\gamma = 0.497\text{ MeV}$) and ¹⁰⁵Ru ($t_{1/2} = 35\text{ h}$, $E_\gamma = 0.73\text{ MeV}$). The former nuclide is preferably counted [26]. Instrumental NAA is precluded in the presence of U, the fission of which produces $0.14\ \mu\text{g}$ of ¹⁰³Ru per microgram of U. Separation of Ru prior to irradiation is recommended [27–30].

Other techniques

ICP AES offers a DL of 30 ng ml^{-1} at the most sensitive 240.272 nm line [11]. Formation of volatile RuO₄ in the solution (by addition of KIO₄ or Ce(IV)) results in a 70-fold increase in sensitivity because of the improved transport efficiency [31]. Ruthenium has seven stable isotopes: ⁹⁶Ru (5.52%), ⁹⁸Ru (1.86%), ⁹⁹Ru (12.74%), ¹⁰⁰Ru (12.6%), ¹⁰¹Ru (17.05%), ¹⁰²Ru (31.57%) and ¹⁰⁴Ru (18.66%). ICP MS offers a DL of 0.07 ng ml^{-1} [32,33]. The ¹⁰¹Ru is overlapped by SrOH [34]. Use of ETV with Ni as a matrix modifier has been reported [33].

47.3 ANALYSIS OF REAL SAMPLES

Because of an extremely complex solution chemistry the standardization of Ru stock solution prior to use is of vital importance and has been discussed in detail [35]. Sample dissolution bears a risk of volatilization losses of RuO_4 . Use of HClO_4 or *aqua regia* for non-distillation procedures is precluded. A reflux heating or the use of pressure bombs is mandatory to avoid losses. In the classical lead fire assay quantitative collection of Ru is seriously affected by flux composition and assay conditions. Cupellation in a silver or gold bead is invalid as Ru is lost. Ruthenium is collected quantitatively in Pt and Pt–Rh (13%) beads. NiS fire assay allows quantitative recovery of Ru [9,30,32,33]. An alternative is fusion with Na_2O_2 alone or with additions of alkali carbonates, hydroxides and borates [8,11,36]. A detection limit of 1 ng g^{-1} in ores has been reported in a review paper [37]. Methods for the determination of Ru are summarized in Table 47.1.

TABLE 47.1

Methods for trace determination of ruthenium

Material (amount)	Sample decomposition	Separation	Determin. technique	DL (ng/g)	Ref.
Rocks, ores (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	NAA	3	9
Rocks	NiS fire assay, the bead dissolved in HCl	none	ID ETV ICP MS	n.g.	33
Sand, rocks, ores (25 g)	NiS fire assay	none	INAA	200	28, 29
CRMs (20–30 g)	NiS fire assay, the bead dissolved in HCl	none	ICP MS	0.1	32
Rocks, ores (50 g)	NiS fire assay	none	INAA	3	30
Ores (50 g)	NiS fire assay, the bead dissolved in HCl	none	GF AAS	0.015 ^a	30
Meteorites (1 g)	HNO_3 –HCl (reflux)	volatn. from H_2SO_4 containing CrO_3 , trapping in NaOH	NAA	n.g.	26

Material (amount)	Sample decomposition	Separation	Determin. technique	DL (ng/g)	Ref.
Meteorites (1 g)	HCl (reflux)	oxidn. with NaIO ₄ , extrn. as RuO ₄ (CHCl ₃)	GF AAS	0.1	7
Ores, mattes, concentrates, (2 g), rocks (5 g)	<i>aqua regia</i> -HF; the residue fused with Na ₂ O ₂	copptn. with Te	GF AAS	30 ^c	10
CRMs coal, rock	fusion with NaOH-Na ₂ O	extrn. of RuO ₄ (CCl ₄)	NAA	1-9 ^b	8
Rocks (0.5 g)	fusion with LiBO ₂	sorption on polyDDTC resin	ICP AES	10-20	36
Sweeps	fusion with Na ₂ CO ₃ -Na ₂ O ₂ or NiS fire assay, the sulphide dissolved in <i>aqua regia</i> -HF	sepn. of Ag with HCl; pptn. of Ru ⁰ with formic acid	AAS ICP AES DCP AES	0.5 ^a	11
Platinum	<i>aqua regia</i> (bomb)	extrn. of the matrix into i-AmOH-MIBK	GF AAS	2000	25

^a In µg/ml in solution; ^b absolute detection limit, pg; ^c sensitivity, pg.

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Scandium

Scandium (Sc, atomic weight 44.96, melting point 1539°C, $d = 3.0 \text{ g cm}^{-3}$) is a soft, silvery-white metal. It occurs in the earth's crust with an average abundance of 25 ppm, usually accompanying uranium ores. The metal reacts readily with water. In aqueous solution, it occurs exclusively in the III oxidation state, primarily as Sc^{3+} which tends to hydrolyze and to form polymeric species. The hydroxide, $\text{Sc}(\text{OH})_3$, precipitates at pH above 4.8 is amphoteric and dissolves in excess alkali to give the tetrahydroxoscandate anion, $\text{Sc}(\text{OH})_4^-$. Scandium forms stable fluoride (ScF_6^{3-}), sulphate, thiocyanate, ascorbate and oxalate complexes. In some chemical properties, Sc resembles the lanthanides and in others aluminium.

48.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of Sc as the thiocyanate complex into diethyl ether allows its separation from the REEs. This can also be achieved by extracting Sc and REEs with TOPO and stripping the REEs into the aqueous phase [1]. Scandium can also be extracted as the ascorbato complex with Aliquat 336S [2]. Several extraction reagents (solvents) proposed included 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (benzene) [3], methyltriocetylammmonium chloride (xylene) [4], crown ethers (CH_2Cl_2) [5], acetylacetone [6]. Substoichiometric extraction of Sc with Alizarine into octanol has been proposed [7].

Ion exchange

The anionic Sc sulphate complex is retained by anion exchangers and passes through cation exchangers. Matrix effects in the separation of Sc

by cation exchange have been discussed [8]. Scandium can be separated from REEs by ion interaction chromatography of nitriloacetato complexes in the presence of 1-octanesulphonate [9].

48.2 DETERMINATION TECHNIQUES

Spectrophotometry and fluorometry

The colour reaction of Sc with Xylenol Orange in a slightly acidic medium is the basis of the most popular spectrophotometric method ($\epsilon = 2.9 \times 10^4$ at 565 nm). Many anions and cations interfere. Triphenyl-methane dyes, e.g. Chrome Azurol S or Eriochromocyanine R in the presence of surfactants, e.g. Zephiramine or cetylpyridinium, offer very high sensitivities ($\epsilon \approx 1 \times 10^5$) and are selective *vs* Y and the lanthanides. Fluorometric methods allow DLs down to 0.2 ng ml^{-1} to be reached and have been reviewed [10]. The example reagents include quinizarine [11] and 1,2,7-trihydroxyanthraquinone [4].

Atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.3 \text{ } \mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O-C}_2\text{H}_2$, reducing (rich, red) flame at the most sensitive 391.2 nm line. Ionization should be controlled by the addition of 0.1% or more of KCl. The Sc signal is reduced in the presence of sulphate and fluoride so matrix matching is necessary. Graphite furnace AAS fails for Sc albeit it was reported for its determination as part of a multielement analysis scheme [12]. Electrothermal atomization of Sc from graphite and tantalum surfaces has been discussed [13].

Atomic emission spectrometry

Scandium was determined by flame ($\text{N}_2\text{O-C}_2\text{H}_2$) AES with a high resolution monochromator with a DL of $10\text{--}15 \text{ ng ml}^{-1}$ [14]. Inductively coupled plasma AES offers DLs down to 1 ng ml^{-1} at the most sensitive 361.38 and 357.25 nm lines. Spectral interferences in the determination of Sc in pure Ce, Nd and La matrices have been discussed [15]. Application of a wall-stabilized plasma arc AES has been reported [16].

Neutron activation analysis

Neutron activation analysis is based on the reaction $^{45}\text{Sc}(n,\gamma)^{46}\text{Sc}$ and counting the ^{46}Sc ($t_{1/2} = 85 \text{ d}$, $E_\gamma = 0.89$ and 1.12 MeV) [17,18]. A chemical separation is required in the presence of long-lived radionuclides (e.g. ^{59}Fe , ^{60}Co , $^{110\text{m}}\text{Ag}$). A DL down to 0.04 ng was reported [18].

Mass spectrometry

Scandium is monoisotopic (^{45}Sc). The determination by ICP MS is hampered by the interference with CO_2H [19].

TABLE 48.1

Methods for the determination of scandium

Sample (amount)	Decomposition	Separation and/or preconcentration	Determin. technique	DL ($\mu\text{g/g}$)	Ref.
Mineral water	none	cation exchange	ICP AES	0.0005	20
Fly ash	evaporn. with HF, dissoln. in HCl or $\text{HNO}_3\text{--H}_2\text{O}_2$	extrn. with methyl- trioctylammonium chloride (xylene)	GF AAS	100 ^a	21
Fly ash, geoCRMs (0.25 g)	$\text{HNO}_3\text{--HClO}_4\text{--HF}$ (bomb)	none	GF AAS	0.8	22
Fly ash, geoCRMs (0.25 g)	fusion with LiB_4O_7 , dissoln. in HNO_3	none	ICP AES	0.6	22
GeoCRMs (0.2 g)	fusion with $\text{K}_2\text{CO}_3\text{--}$ $\text{K}_2\text{B}_4\text{O}_7$	none	ICP MS	0.1	23
GeoCRMs (0.1 g)	n.g.	cation exchange	GF AAS	<0.001	12
GeoCRMs (0.3 g)	$\text{HF--HClO}_4\text{--HNO}_3$, the residue fused with $\text{Li}_2\text{B}_4\text{O}_7$	none	ICP AES	<1	8
Geo??	$\text{HNO}_3\text{--HF}$	extrn. with Alizarine (octanol)	NAA	10 ^b	7
Rocks (0.1 g)	$\text{HF--H}_2\text{SO}_4$ or fusion with LiBO_2	none	FLU	2 ^a	4
W-ores (0.5 g)	fusion with Na_2O_2 , dissoln. with HCl	extrn. with 1- phenyl-3-methyl-4- benzoyl-pyrazol-5- one (benzene)	VIS	n.g.	3
Milk, body fluids, soil	dry ashing		INAA	0.0001	18

^a In the solution fed, ng/ml; ^b absolute detection limit, ng.

48.3 ANALYSIS OF REAL SAMPLES

The virtual lack of the need of trace determination of Sc is responsible for the scarcity of methods in the literature developed with the objective of solving a real analytical problem. Applications, summarized in Table 48.1, refer primarily to geochemical materials. Scandium is often determined in the multielement array by ICP AES (*cf.* Part II).

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Selenium

Selenium (Se, atomic weight 78.96, melting point 221°C, $d = 4.79 \text{ g cm}^{-3}$) exists as the grey-black hexagonal allotropic form. It occurs in the earth's crust with an average abundance of 0.09 ppm. The element dissolves in HNO_3 to form SeO_3^{2-} and in concentrated H_2SO_4 . Selenium is commonly found in oxidation states -II, IV, VI. On boiling, HCl reduces selenate (SeO_4^{2-}) to selenite (SeO_3^{2-}). Strong oxidants, e.g. MnO_4^- , H_2O_2 and Br_2 oxidize SeO_3^{2-} to SeO_4^{2-} . Elemental Se is precipitated from SeO_3^{2-} solutions by SnCl_2 , NH_2OH , N_2H_4 , NaBH_4 and Zn. Selenium can be both essential and toxic depending on the species and concentration present. The need for the analysis and speciation of selenium is driven by the release of Se in the environment from fossil fuel combustion and industrial discharges, and its involvement in biochemical processes. Organoselenium species usually determined include dimethylselenide (DMSe), dimethyldiselenide (DMDS), dimethyl selenone, selenomethionine (SeME), selenocysteine (SeCYS), trimethylselenonium (TMeSe^+) and macromolecular selenoproteins.

49.1 SEPARATION AND PRECONCENTRATION

Volatilization

Hydrogen selenide is formed by reduction of Se(IV) with NaBH_4 in strong acid media. Selenium (VI) needs to be reduced to Se(IV) beforehand, usually with boiling 4–7 M HCl [1–9]. To avoid the back-oxidation of Se(IV) by the residual Cl_2 , the system should be flushed with an inert gas during the process [10]. If present, H_2Se should be stripped at low pH to avoid dissociation [11]. The efficiency of the Se(IV) reduction with NaBH_4 is increased if iodide [12–14] or bromide [15] is present during

the reduction step. The interference with Cl_2 is eliminated and the reaction is accelerated by using a HBr medium for prereduction and hydride generation [16,17]. Electrochemical generation of H_2Se has been reported [18]. The generation of H_2Se is interfered with by many metals, the fine precipitates of which formed upon reduction with NaBH_4 can capture and decompose the H_2Se . Other interferents include hydride-forming elements, which compete for the reagent, and redox species. Interferences have been comprehensively discussed [19]. The mechanisms have been studied with emphasis on bivalent metals (Sn(II) , Ni , Co , Cd , Zn , Fe(II)) [20,21] and Cu , Ag and Au [22]. Interferences can be alleviated by increasing the HCl and decreasing the NaBH_4 concentrations (masking of interfering ions as chlorocomplexes) [5,23], masking with 1,10-phenanthroline [9,24] or hexacyanoferrate(III) [25] or addition of Fe(III) that acts as a redox buffer [5,26]. The most troublesome is the interference with Cu [20,23,27]. It can be removed by preseparation [2,4,8,27–30] or by masking [13,18,31] of Cu . Serious problems also occur with Ni which should be masked with citric acid [32] or removed [4,29,30]. Lead can be precipitated as PbCl_2 [33]. The sources of systematic errors in HG AAS have been studied by the radiotracer technique [10]. Various semiautomated or automated CF of FI systems for hydride generation have been developed [4,5,9,24,34–36]. Experimental DLs can be enhanced by trapping the H_2Se in a Pd -modified graphite furnace [3,37] or cryogenically on a GC packing [31]. The memory effects related to the deposition of unreacted analyte, metal selenides (e.g., CuSe), or H_2Se on the surface of the Teflon mixing tube and gas–liquid separator have been discussed [38]. Other volatilization methods include distillation of SeBr_4 or SeCl_4 from conc. HBr and HCl , respectively, and formation of volatile species by reaction of Se(IV) with NaBEt_4 [39] or 1,2-diaminobenzene and its derivatives [40,41].

Coprecipitation

Elemental Se can be precipitated with various collectors, e.g. As , Cu , Te , Pd upon reduction with hypophosphorous or ascorbic acid [33, 42–44], or electrochemically on a Pt wire [45]. Selenium (IV) can be coprecipitated with La(OH)_3 as a collector [15,46,48], and also *on line* [47]. Precipitation as dibenzylthiocarbamate with phenolphthalein [48] and with $\text{Ni-pyrrolidinedithiocarbamate}$ [49] has been reported.

Extraction

Selenium(IV) has been extracted as SeI_4 into toluene [50,51]. Piazselenols formed by reaction of Se(IV) with 1,2-diaminobenzene or 2,3-diaminonaphthalene or its derivatives are readily extractable into nonpolar solvents [52–57]. Extraction of Se(IV) with dithiocarbamates while interferents are masked with ascorbic acid is an alternative [58].

Sorption

Sorption of Se on thiol cotton fiber [59], Bismuthiol II sulphonate [60] and anion-exchange resins [25] has been reported. Sorption of the Se-APDC complex on activated carbon is an alternative [61].

49.2 DETERMINATION TECHNIQUES

Spectrophotometry and spectrofluorimetry

The most widely used is the method based on the reaction of Se(IV) with 3,3'-diaminobenzidine to form the yellow piazselenol either in aqueous phase or on extraction into toluene ($\epsilon = 1 \times 10^4$ at 420 nm). Fluorimetric methods are based on the fluorescent Se(IV) complex with naphthalene-2,3-diamine [62,63] which is also used for derivatization of LC effluents [64]. Catalytic determination based on the Se-catalyzed reduction of substituted tetrazolium bromide was reported to give a DL 0.1 ng ml^{-1} [60].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.6 \text{ } \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 oxidizing (lean, blue) flame at the 196.1 nm line [2]. Because of considerable scattering of the radiation background correction is essential to improve the signal-to-noise ratio. An EDL is *ca* 25% more sensitive than an HCL.

Quartz furnace atomic absorption spectrometry

Quartz furnace AAS offers a DL of 0.02 ng ml^{-1} [34]. The role of sodium borohydride and of hydride gas [65] as well as that of oxygen and of the cuvette wall [66] in the determination of Se by HG AAS has been discussed. The HG QF AAS determination of Se has been optimized using experimental designs [67].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of 10 pg. Iron is the major interferent with the D_2 correction due to the formation of FeO in the presence

of oxygen and the risk of overcorrection. The remedies include either Zeeman background correction or the addition of CO (as O₂ scavenger) and Pt (as catalyst) [68]. Other important spectral interferences include Ni [69] which can be corrected by the Zeeman effect, and phosphorus [70]. Deuterium correction may not compensate for the background of Ca and Mg phosphates, so for the routine analysis Zeeman correction should be used [71]. Volatility losses are pertinent. Selenium can be lost during drying (if present as some organoselenium compounds) and during ashing and atomization owing to formation of volatile H₂Se or SeO₂. The thermal behaviour is dependent on the oxidation states [72]. Atomization and interference mechanisms have been studied [73–76]. Matrix modification is always required. Nickel stabilizes Se(IV) and Se(VI) in the presence of NaCl and Na₂SO₄ [73,77] and also converts the interfering PO⁺ into free P atoms [78]; the mechanisms have been discussed in detail [74]. Nickel alone is insufficient for organic matrices [79,80]; combination of Ni with Pt [81], Ag [82] and with Mg(NO₃)₂ [83,84] has been proposed. Palladium [44,58,59], especially when applied with Mg(NO₃)₂, was found to be more suitable [85–92]. The efficiency of the Pd modifier increases in the presence of ascorbic acid [93,94]; the mechanism has been elucidated [87]. Other modifiers included Pt(IV)–Mg(NO₃)₂ [95], Rh–Mg(NO₃)₂ [96], Pt–Cu [81], Cu [97], CdCl₂–PdCl₂ [98] and PdCl₂ [7]. The sulphate interference can be overcome by the addition of Ba(NO₃)₂ [90,99]. Graphite tubes coated pyrolytically [81,94,97], with Ta [58] or Ag [100] are recommended. Chlorides and nitrates of Mg, Ca and Al were found to give similar interferences during the atomization of Se from both the tube wall and L'vov platform [101].

Atomic emission spectrometry

A DL of 30 ng ml⁻¹ is obtained with ICP AES at the most sensitive 196.026 nm line. Iron interferes and must be separated. A 50–100-fold increase in sensitivity and elimination of spectral interferences is achieved by HG ICP AES. Systems of various degree of automation have been developed [8,102–105]. Other emission techniques include hollow-cathode discharge AES [106] and HG DCP AES [19,24].

Fluorescence

Non-dispersive AFS with atomization of H₂Se using a combined electrothermally heated quartz tube–flame atomizer offers a DL of ca 0.03 ng [16,17,107]. Electrothermal LE AFS offers an ADL of 15–80 fg

and with $\text{Pd}(\text{NO}_3)_2$ as matrix modifier can be applied to various samples [108]. Selenium can be determined by WD XRF with an ADL of 0.1 μg , usually after separation [6,43,109]. Use of TXRF with synchrotron excitation has been reported [110].

Neutron activation analysis

The long-lived ^{76}Se ($t_{1/2} = 127$ days, $E_\gamma = 0.14$ and 0.27 MeV) and short-lived $^{81\text{m}}\text{Se}$ ($t_{1/2} = 56.6$ min, $E_\gamma = 0.10$ MeV) are the principal Se nuclides used for NAA. A radiochemical separation is required because of poor sensitivity and interferences, e.g. with ^{32}P [62]. Radiochemical NAA offers a DL of ca 0.5 $\mu\text{g g}^{-1}$ for solid samples [62].

Mass spectrometry

Selenium has six stable isotopes: ^{74}Se (0.88%), ^{76}Se (8.95%), ^{77}Se (7.65%), ^{78}Se (23.51%), ^{80}Se (49.62%) and ^{82}Se (9.39%). Thermal ionization ID MS in the negative ion mode is widely applied [111–114]. The ^{82}Se (enriched) to ^{80}Se ratio is typically measured. Since the major isotopes (^{80}Se , ^{78}Se and ^{76}Se) are interfered by Ar dimers in ICP MS, the minor ones, especially ^{77}Se , must be used [1]. The $^{40}\text{Ar}^{37}\text{Cl}^+$ interference can be reduced by the addition of small amounts of an alcohol [115,116] or a molecular gas (e.g. N_2 or O_2) [115,117,118], or by removal of Cl^- by gel or membrane filtration [62,119], anion exchange [120,121] or *on-line* ASV [122]. A mathematical correction for spectral interferences has been discussed [123]. Hydride generation ICP MS [1,13,38,62,124,125] offers DLs down to the low pg/ml level [38,62] and is a factor of 100 more sensitive than the conventional nebulization ICP MS [125]. Isotope dilution has been widely used for quantification [38,83,126]. Isotope dilution GC MS of piarselenol complexes has been reported [41].

49.3 ANALYSIS OF REAL SAMPLES

Digestion procedures are prone to losses [72] which can be prevented by pressure decomposition or the use of reflux. Several organoselenium compounds can be lost on drying. Some organoselenium compounds such as SeME , SeCYS , TMSe^+ are very resistant to acid attack. SeME and TMSe^+ can only be converted into Se(IV) after $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--HClO}_4$ treatment at 310°C [127]. UV photooxidation which requires less time and minimizes the risk of losses is an alternative method to convert organoselenium into Se(IV) . Combustion in pure O_2 converts Se

into volatile SeO_2 which is then cryofocused [97,128]. A list of CRMs can be found elsewhere [129]. Methods for the determination of Se in biological samples and water have been critically evaluated [130].

49.3.1 Environmental and geological materials

Air

Gaseous Se forms can be trapped on gold-coated beads or activated charcoal, and then leached with dilute HCl-HNO_3 or thermally desorbed prior to GF AAS [131,132]. Aerosol Se is analyzed by GF AAS upon dissolution of the filter with $\text{HNO}_3\text{-HClO}_4$ [133].

Water

The Se concentrations range from ng/l and ng/g to ng/ml and $\mu\text{g/g}$ in water and sediment, respectively. Selenium is usually separated by volatilization as H_2Se and analyzed by QF AAS, ICP AES or ICP MS. The H_2Se can be preconcentrated by trapping in a GF prior to AAS [3,37]. Analytical procedures are summarized in Table 49.1.

Geological materials

Selenium can be determined directly in the sample digest by GF AAS [7,98] (with Zeeman or Smith-Heftje correction) but it is more often determined on hydride generation. Wickbold combustion has been investigated for the decomposition of various environmental CRMs [137]. Mixed acid digestion procedures ($\text{HNO}_3\text{-HClO}_4\text{-HF}$, $\text{HNO}_3\text{-H}_2\text{O}_2\text{-HF}$ and $\text{HNO}_3\text{-HCl-HF}$) gave comparable results for Se determination in soils by Zeeman GF AAS and HG AAS [7]. Digestion of soil by H_3PO_4 , HNO_3 and H_2O_2 prior to fluorimetric determination has been discussed [138]. Fluorimetry, HG AAS, HG ICP AES, HG ICP MS and RNAA were evaluated for the analysis of sediments [62]. Methods for the analysis of geochemical materials are summarized in Table 49.2.

49.3.2 Biological materials

Clinical samples.

Selenium in blood ($160\text{--}240\text{ ng ml}^{-1}$) and serum ($70\text{--}120\text{ ng ml}^{-1}$) is preferably determined by GF AAS directly (upon dilution) to minimize the risk of contamination [139–142]. A cooperative study on measurement of selenium in freeze-dried human whole blood was published [143]. Selenium in blood and serum occurs primarily as Se(-II) in protein-bound forms and in urine as methylated forms which show a

TABLE 49.1

Determination of selenium in water

Water (amount)	Sample preparation	Detection	DL (ng/l)	Ref.
CRM sea	evaporation with $\text{H}_2\text{SO}_4\text{--HClO}_4$, volatilization as H_2Se	ICP AES	400	105
CRM sea (100 ml)	volatilization as H_2Se	ICP MS	2.5	38
CRM (10 ml)	volatilization as H_2Se	ICP MS	6	1
CRM sea (300 ml)	sorption on C_{18} as APDC complex, elution with MeOH	GF AAS	7	134
CRM sea (20–50 ml)	volatilization as H_2Se , trapping in a GF	GF AAS	1.5	37
CRM sea	volatilization as H_2Se	ND AFS	27 ^a	16
CRM sea, drinking, swimming pool (5 ml)	volatilization as H_2Se	ND AFS	n.g.	17
Sea (0.25–0.5 l)	coprecipitation with $\text{La}(\text{OH})_3$, volatilization as H_2Se	QF AAS	8	46
Fresh (100 ml)	anion exchange after digestion with KMnO_4 at pH 2, volatilization as H_2Se	FI AAS	5	135
Fresh	coprecipitation with DBDTC and phenolphthalein	INAA		48
Fresh (250 ml)	precipitation of Se^0 or volatilization as H_2Se	ID TIMS	10	111
River (50–500 ml)	evaporation with $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--}$ HClO_4 , volatilization as H_2Se	QF AAS	n.g.	29
River	volatilization as H_2Se	QF AAS	1000	34
Lake, waste	volatilization as H_2Se , trapping in a GF	GF AAS	n.g.	3
Drinking, mineral, river, rain	volatilization as H_2Se , trapping on Chromosorb W	QF AAS	6 ^a	31
Tap, well (6.7 ml)	on-line copptn. with $\text{La}(\text{OH})_3$, volatilization as H_2Se	FI AAS	1	47
Ground (200 ml)	anion exchange of $\text{Se}(\text{IV})$ and $\text{Se}(\text{VI})$	ID TIMS	40	112
Mineral (5–25 ml)	volatilization as H_2Se	QF AAS	n.g.	136

^a Absolute detection limit, pg.

TABLE 49.2

Determination of selenium in geological samples

Sample (amount (g))	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
CRM fly ash (0.1)	<i>aqua regia</i> -HF (microwave assisted)	volatilization as H ₂ Se	ND AFS	27 ^a	16
CRM fly ash (0.2), soil (0.5)	HNO ₃ -HClO ₄ - HF or HNO ₃ - H ₂ O ₂ -HF or HNO ₃ -HCl-HF	volatilization as H ₂ Se	AAS	n.g.	7
CRM fly ash (0.5)	HNO ₃ -HClO ₄	none	GF AAS	7 µg	98
Fly ash, soils, sediments, rocks (2)	HClO ₄ -HNO ₃ , HF	extraction as piaselenol (toluene)	GF AAS	10	54
Fly ash, sludge (0.05-0.1)	HCl-HNO ₃ (leaching)	volatilization as H ₂ Se	QF AAS	n.g.	6
CRM rocks (0.2)	HF-HClO ₄ - HNO ₃	volatilization as H ₂ Se	FI QF AAS	n.g.	9
Ores, soil, rocks, CRMs (0.2)	HF-HClO ₄ - HNO ₃	sorption on thiol cotton, digestion with HCl-HNO ₃	GF AAS	n.g.	59
CRM marine sediments (0.5)	HF-HClO ₄ - HNO ₃ (bomb)	volatilization as H ₂ Se, trapping in a GF	GF AAS	30	37
CRM sediments	HNO ₃ -HF (bomb)	volatilization as H ₂ Se	ID TIMS	6	114
Estuarine sediments (1.0)	HNO ₃ -HClO ₄ - H ₂ SO ₄	volatilization as H ₂ Se	QF AAS	n.g.	5

^a Absolute detection limit, pg.

different thermal behaviour from inorganic selenium. Chemical modification and spectral interferences in Se determination in whole blood and urine (0.1 µg ml⁻¹) have been discussed [70]. Platform atomization, Zeeman correction (alleviation of the Fe and PO₄³⁻ interferences) and Ni modifier [141,144] with ashing temperatures from 300 to 1200°C offer a DL of 10 ng ml⁻¹. Other modifiers used included Cu(NO₃)₂-Mg(NO₃)₂

[145], Pd-ascorbic acid [93,146], $\text{Ni}(\text{NO}_3)_2$ - $\text{Pd}(\text{NO}_3)_2$ for urine [91], $\text{Ni}(\text{NO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ [83], Ni-Pt (D_2 correction) [81]. Various modifiers for simultaneous determination of different Se compounds by ETA ZAAS have been compared [147]. Hydride generation AAS can be successfully used (*cf.* Table 49.3) but it is inconvenient because any oxidative digestion pushes Se to Se(VI) which must then be reduced, and the accuracy of the determination depends critically upon the way of sample decomposition [140,148]. Other techniques included fluorimetry [63], ED XRF [110] and hollow-cathode discharge AES following *in-situ* preconcentration by drying the sample onto the wall of an Al-cathode cup ($\text{DL } 1 \text{ ng ml}^{-1}$) [106]. Digestion of plants by H_3PO_4 , HNO_3 and H_2O_2 prior to fluorimetric determination has been discussed [138]. Both digestion with HNO_3 - HClO_4 and microwave digestion with HNO_3 - H_2O_2 under reflux were found to be suitable for plasma, blood and urine [41]. Combined procedures for the analysis of clinical samples are summarized in Table 49.3.

Other biomaterials

Selenium in bovine blood was subject of an intercomparison study [151]. Direct GF AAS: cup-in-tube [86] or on dilution [152] using STPF with Pd-based modifiers and Zeeman correction, has been used for plant and animal tissues [152]. As the behaviour of various Se species during the ashing step is unpredictable, predigestion in harsh conditions is generally recommended. Wet mineralization with HNO_3 - HClO_4 [3,45, 63,78,153] and HNO_3 - HClO_4 - H_2SO_4 [149,154], HNO_3 - H_2SO_4 [150, 154] are most frequently used. Volatilization losses are reduced by the addition of $\text{Mg}(\text{NO}_3)_2$ [13,37,38,43,149,155]. Pre-digestion with HNO_3 followed by open-flask or microwave digestion with H_2SO_4 - HClO_4 is an alternative [58,105,155]. Pressure digestion with HNO_3 , HNO_3 - H_2SO_4 - HClO_4 , HNO_3 - $\text{Mg}(\text{NO}_3)_2$ and HNO_3 - HClO_4 and closed flask O_2 combustion were found to be effective for bovine liver provided that the standard additions method was used [36,156]. A microwave procedure for drying and HNO_3 extraction of Se from fish tissue has been recommended [157]. Four microwave digestion methods for the determination of Se in fish tissue by HG AAS have been compared and the HNO_3 - H_2SO_4 - H_2O_2 mixture was found to be the best [25]. Graphite furnace AAS is the most widely used determination technique [71,78,84,89, 95,158,161]. Matrix modification is vital. The modifiers proposed included: Pt(IV)- $\text{Mg}(\text{NO}_3)_2$ [95], $\text{Ni}(\text{NO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ [84], $\text{Pd}(\text{NO}_3)_2$ - $\text{Cu}(\text{NO}_3)_2$ [158] and Ni [78]. Slurry GF AAS of milk powder with a Rh- $\text{Mg}(\text{NO}_3)_2$ matrix

TABLE 49.3

Combined procedures for the determination of Se in clinical materials

Sample (amount)	Digestion	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Body fluids (0.1–1 ml)	$\text{HNO}_3\text{--H}_3\text{PO}_4$, H_2O_2	volatilization as H_2Se	AAS	n.g.	63
Body fluids (0.2–1 ml), urine (1 g)	$\text{HNO}_3\text{--HClO}_4$	extraction with 2,3-naphthalene- diamine (cyclo- hexane)	fluorimetry	n.g.	63
Serum (2 ml)	$\text{HNO}_3\text{--H}_2\text{SO}_4\text{--}$ HClO_4	volatilization as H_2Se	FI QF AAS	1.2 ^a	35
Serum, blood, urine	$\text{HNO}_3\text{--H}_2\text{O}_2$ or $\text{HNO}_3\text{--HClO}_4$	volatilization as H_2Se	ICP MS	n.g.	24
Serum, blood, urine (0.1–1 ml)	$\text{HNO}_3\text{--HClO}_4$ or $\text{HNO}_3\text{--H}_2\text{O}_2$ (microwave assisted, reflux)	extraction with 4- nitro- <i>o</i> -phenylene- diamine (CHCl_3)	ID GC MS	2 ^a	41
Serum, hair, nails (0.3–5 mg)	$\text{HNO}_3\text{--HClO}_4$ (bomb), HCl	volatilization as H_2Se , trapping on a sorbent	QF AAS	6 ^b	31
Blood (0.5 g), urine (1 g)	$\text{Mg}(\text{NO}_3)_2\text{--}$ $\text{HNO}_3\text{--HCl}$ or $\text{HNO}_3\text{--HClO}_4\text{--}$ H_2SO_4	volatilization as H_2Se	QF AAS	n.g.	149
Blood	$\text{HNO}_3\text{--HClO}_4$, MgCl_2	extraction with <i>o</i> - phenylenediamine (toluene)	RNAA	500	52
Human tissue (0.1–0.2 g)	$\text{HNO}_3\text{--H}_2\text{SO}_4$	volatilization as H_2Se	QF AAS	n.g.	150
Breast tissue	<i>aqua regia</i> – HClO_4	extraction with <i>o</i> - phenylenediamine (benzene)	RNAA		53
Hair (0.5 g)	HNO_3	extraction as SeI_4 (toluene)	GF AAS	n.g.	50
Hair, bioCRMs, urine (0.5–1.0 g)	HNO_3	volatilization as H_2Se	DCP AES	0.5 ^a	24
CRM urine (20 μl)	$\text{HNO}_3\text{--HClO}_3$ (bomb)	volatilization as H_2Se , trapping in a GF	GF AAS	n.g.	3

^a In the solution fed, ng/ml; ^b absolute detection limit, pg.

modifier was reported to give a DL of 26 ng g^{-1} [96]. Fluorimetry has been recommended for Se concentrations below $0.3 \text{ } \mu\text{g g}^{-1}$ and INAA for levels above this limit [159]. Determination of selenium in foodstuffs has been discussed [160]. Combined procedures for the analysis of non-clinical biomaterials are summarized in Table 49.4.

TABLE 49.4

Determination of selenium in non-clinical biological materials

Sample (amount)	Digestion	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Plant	$\text{HNO}_3\text{--HClO}_4$	volatn as H_2Se , cryotrapping	QF AAS	n.g.	153
Plant (1 g)	$\text{HNO}_3\text{--HClO}_4\text{--HF}$	volatn. as H_2Se	FAAS	0.9^a	18
Plant (0.4 g)	combustion in O_2	trapping in $\text{CH}_3\text{COOH--H}_2\text{O}_2$	GF AAS	0.003	97
Plant, animal tissues (0.5–1 g)	HNO_3 , $\text{H}_2\text{SO}_4\text{--HClO}_4$ (microwave assisted)	extrn. as DDTC complex (CHCl_3)	GF AAS	0.002	58
CRM plant (1 g)	$\text{HNO}_3\text{--Mg(NO}_3)_2\text{--Ni(NO}_3)_2$	copptn. with Te	WD XRF	0.1	43
CRM plant, flour	HNO_3 , $\text{HNO}_3\text{--H}_2\text{SO}_4\text{--HClO}_4$	volatn. as H_2Se	QF AAS	n.g.	29
BioCRMs, foodstuffs, faeces (5 g), urine (7.5 g)	$\text{HNO}_3\text{--H}_2\text{SO}_4$	volatn. as H_2Se	QF AAS	n.g.	154
BioCRMs (0.2 g)	$\text{HNO}_3\text{--HClO}_4$ or $\text{HNO}_3\text{--H}_2\text{O}_2$ (microwave assisted, reflux)	extrn. with 4-nitro- <i>o</i> -phenylenediamine (CHCl_3)	ID GC MS	2^a	41
BioCRMs (0.1–0.2 g)	$\text{HNO}_3\text{--H}_2\text{SO}_4$	volatn. as H_2Se	QF AAS	n.g.	150
BioCRMs	$\text{HNO}_3\text{--HClO}_4$ (bomb), HCl	volatn. as H_2Se , trapping on a sorbent	QF AAS	6^b	31
BioCRMs (1.0–1.5 g)	HNO_3 , $\text{HClO}_4\text{--H}_2\text{SO}_4$	volatn. as H_2Se	ICP AES	0.004	105

continued

TABLE 49.4 (continuation)

Sample (amount)	Digestion	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
BioCRMs (1–2.5 g)	$\text{HNO}_3\text{--H}_2\text{SO}_4\text{--V}_2\text{O}_5$ or $\text{HNO}_3\text{--HClO}_4$	electrodeposition	GF, FAAS	n.g.	45
BioCRMs (0.1–1 g)	$\text{HNO}_3\text{--Mg}(\text{NO}_3)_2$	volatn. as H_2Se	ID ICP MS	1.3 ^a	13
BioCRMs (1.0–1.5 g)	HNO_3 , $\text{HClO}_4\text{--}$ H_2SO_4	volatn. as H_2Se	ICP AES	0.004	105
Foodstuffs (0.15 g)	HNO_3 (bomb)	volatn. as SeBr_4 , pptn. as Se^0	RNAA	n.g.	160
Wine	$\text{HNO}_3\text{--HClO}_4$	volatn. as H_2Se	QF AAS	20 ^b	162
Biotissues	HNO_3 (bomb)	sorption of APDC complex on activated carbon	INAA	100 ^a	61
Biotissues	HNO_3 (bomb)	pptn. with ascorbic acid	NAA	n.g.	42
Animal tissue (0.5 g)	$\text{HNO}_3\text{--HClO}_4$	extrn. as diamino- naphthalene complex	ED XRF	100 ^a	57
CRM animal tissue	$\text{HNO}_3\text{--HClO}_4$	volatn. as H_2Se , absorption in HNO_3	ID TIMS	n.g.	113
CRM marine (0.1 g)	HNO_3 , $\text{H}_2\text{SO}_4\text{--}$ H_2O_2	volatn. as H_2Se	AAS	0.3	25
CRM marine	n.g.	n.g.	ND AFS	27 ^b	16
CRM marine (0.5 g)	$\text{HNO}_3\text{--Mg}(\text{NO}_3)_2$, dry ashing	volatn. as H_2Se	QF AAS	0.04	155
CRM marine (0.1 g)	HNO_3 (bomb)	volatn. as H_2Se	ND AFS	n.g.	17
CRM marine (1–2 g)	$\text{HNO}_3\text{--Mg}(\text{NO}_3)_2$	volatn. as H_2Se	ICP MS	0.003 ^c	38
CRM marine (0.5 g)	$\text{HNO}_3\text{--Mg}(\text{NO}_3)_2$	volatn. as H_2Se , trapping in a GF	GF AAS	0.04	37
CRM marine	$\text{HNO}_3\text{--HClO}_4$	sorption on a Bis- muthiol II loaded resin	catalytic photometry	0.1 ^c	60

^a Absolute detection limit, ng; ^b absolute detection limit, pg; ^c in the solution, ng/ml.

49.3.3 Industrial samples

Even trace levels of Se in high purity copper can significantly alter its conductivity and malleability [164]. Nickel metal reacts vigorously with HCl so care should be taken to avoid losses of Se during the dissolution of samples [30]. Interference from Fe during the analysis of steel by FAAS can be minimized by appropriate instrumental settings [164]. Lead matrix has been removed by precipitation as chloride [33]. Selenium in coal can be determined by slurry GF AAS provided that $\text{Ni}(\text{NO}_3)_2$ as a matrix modifier is used. A careful optimization of the GF programme is required to prevent losses and Smith–Heftje background correction to correct for Fe spectral overlap is required [165]. Digestion of coal with HClO_4 [15], HNO_3 [55] or H_2SO_4 – HNO_3 [12] is mandatory if a preconcentration step is involved. Methods for the analysis of industrial materials are summarized in Table 49.5.

49.4 SPECIATION

Hydride generation is the most widely applied technique to differentiate between Se(IV) and Se(VI) (calculated from the difference) in environmental and biological samples (see above). A speciation scheme for fly ash has been proposed [6]. Different chemical forms of Se have been analyzed using stable isotope tracers [166]. Various approaches to species-selective determination of Se have been reviewed [129,167,168]. Analytical methods are summarized in Table 49.6.

Naturally occurring alkylselenium species such as Me_2Se , Me_2Se_2 and Et_2Se are sufficiently volatile to be separated by GC without the need for derivatization [169]. Detection can be *on line* [169] or the alkylselenides can be consecutively adsorbed on the graphite furnace and atomized in the intervals [178].

Trimethylselenonium which is a major metabolism product in higher animals can be separated from inorganic Se anions by cation-exchange chromatography [179–181]. Selenoamino acids are separated by reversed-phase chromatography [182], ion pair [177,183] and capillary electrophoresis [175]. There are about 10 selenoproteins known to exist in mammalian tissues. Size-exclusion chromatography is the preferred method for their speciation. Optimization of HPLC fraction collection AAS has been presented [171]. The LC separation of Se has been reviewed [184].

TABLE 49.5

Determination of selenium in industrial materials

Sample (amount, g)	Dissolution	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
CRM Cu metal, nickel oxide, Cu-Ni alloy (1)	HCl-H ₂ O ₂	matrix removal by pptn. of hydroxides, volatn. as H ₂ Se	QF AAS	n.g.	30
Cu alloys (0.5)	HNO ₃ , HCl	matrix removal by sorp- tion on a chelating resin, volatn. as H ₂ Se	QF AAS	0.1 ^b	4
Cu metal (0.4)	HNO ₃	electrolytic matrix removal volatn. as H ₂ Se	FAAS	n.g.	2
Cu metal (0.5)	HNO ₃	matrix removal by ion exchange, volatn. as H ₂ Se	ICP AES	0.6 ^a	8
Cu metal (0.5)	HNO ₃ , HCl	volatn. as H ₂ Se	FI AAS	2 ^a	27
Pb alloys (2)	HNO ₃ -HClO ₄	matrix pptn. as PbCl ₂ ; pptn. of Se ⁰ with As	GF AAS	n.g.	33
Pb-based alloys (10)	HNO ₃ -HClO ₄	matrix removal by pptn. as PbCl ₂ , volatn. as H ₂ Se	QF AAS	n.g.	33
High purity iron		copptn. with Pd	GF AAS	10	44
Ni metal (0.5)	HCl-HNO ₃ , HCl	matrix removal by sorption on a chelating resin, volatn. as H ₂ Se	QF AAS	0.1 ^b	4
CRM Cu, Zn, Pb concentrates (2)	HClO ₄ -HNO ₃ , HF	extrn. as 5-nitro- piazselenol (toluene)	GF AAS	10	54
CRM coal (0.7)	HClO ₄	copptn. with La(OH) ₃ , volatn. as H ₂ Se	FAAS; FAFS	36 10	15
CRM coal	H ₂ SO ₄ -HNO ₃	volatn. as H ₂ Se	QF AAS	n.g.	12
Coal (500-1000), shampoo (2)	HNO ₃	evaporn. to 1-2 ml, extrn. as 5-nitro- piazselenol (toluene)	HPLC-UV	n.g.	55
Butter (1), polymers (0.6)	ashing in an O ₂ -bomb, digestion with HNO ₃ -H ₂ SO ₄ - HClO ₄	volatn. as H ₂ Se	GF AAS	10	128

^a In the solution, ng/ml; ^b Absolute detection limit in pg.

TABLE 49.6

Speciation analysis of selenium by hyphenated techniques

Analyte	Separation	Mobile phase	Detection	Sample	Ref.
Alkylselenides	GC	helium	MIP AES	water	170
Selenoproteins	SEC	gradient elution with 0-500 IU heparin in 50 mM Tris-HCl buffer, pH 7.4	GF AAS	serum	171
Se(IV), Se(VI), TMSe	AEC	10 and 2 mM ammonium citrate, pH 3.0 and 7.0	GF AAS	urine	172
Se(IV), Se(VI)	AEC	3 mM potassium hydrogen phthalate saturated with Ni(OH) ₂	FAAS	food supplement	173
Se(IV), Se(VI), DMSe	AEC	0.08 M ammonium citrate	ICP AES	standards	174
Se(IV), Se(VI), selenocystine, selenomethionine	CZE	CTA	UV	standards	175
Se(IV), Se(VI)	HPLC	cyclohexane-THF	FLU	river water	56
Selenoproteins	PAGE	sodium dodecyl sulphate	FLU	serum, semen	176
Se(IV), Se(VI)	IIC	5% MeOH, 5 mM NaDS, pH 3.0	ICP MS	standards	177
Selenocystine, selenomethionine	IIC	10 mM tetra- ethylammonium bromide, 1% acetonitrile	GF AAS	white clover	178

CTA = cetyltrimethyl ammonium; FLU = spectrofluorimetry.

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Silicon

Silicon (Si, atomic weight 28.06, melting point 1410°C, density 2.33 g cm⁻³) is a metalloid which can exist either as amorphous dark brown powder or as shiny blackish crystals. Silicon is the second most abundant element in the earth's crust (*ca* 28%), occurring in the form of silica (SiO₂) or silicates. The powder dissolves in HF, hot concentrated HNO₃ and in concentrated alkalis. The main oxidation state of Si is IV. Silicon forms various silicate ions and fluorosilicate. Only the alkali metal silicates are water soluble, the solutions contain colloidal silica and condensed silicate ions in addition to orthosilicate ions. Formation of heteropolyacids with molybdenic acid is analytically important. Silicon forms a homologous series of highly reactive hydrides (silanes) with general formula Si_nH_{2n+2}. Organosilicon chemistry is extensive and its discussion is beyond the scope of this book. The demand for the determination of trace Si is practically restricted to the water, clinical and electronic materials.

50.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Separation and preconcentration are seldom used. Extraction of the molybdosilicic acid from a strongly acidic medium (e.g. 3 M H₂SO₄) with oxygen-containing organic solvents is convenient prior to spectrophotometry. Coprecipitation of Si with Nb as carrier allows its separation from major quantities of P(V), As(V), Fe(III) and Al.

Spectrophotometry

Monosilicic acid reacts with molybdic acid at pH 1–2 to form the yellow soluble β-molybdosilicic acid ($\epsilon = 2.2 \times 10^3$ at 400 nm). In the

presence of reducing agents [e.g. SnCl_2 , Fe(II) or ascorbic acid] the intensely coloured silicomolybdenum blue is formed ($\epsilon = 1.7 \times 10^4$ at 750 nm) [1–3]. The sensitivity can be further increased by the formation of ion-associates with basic dyes which can be separated by flotation ($\epsilon = 4\text{--}5 \times 10^5$ at 590 nm) [4]. The silicomolybdenum blue method is competitive with other techniques as it is sensitive and fairly selective (the interference from arsenate and phosphate is negligible in real sample analyses) and readily adaptable to FIA [1,2,3].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a characteristic mass of 30 pg at the most sensitive 251.6 nm line. At elevated temperatures Si is easily combined with graphite and oxygen to form the refractory carbide and volatile monoxide, respectively [5]. In the presence of sulphur a gaseous monosulphide can be formed [6]. In the absence of modifier Si is lost at pyrolysis temperatures above 1100°C; volatilization losses are particularly acute in the presence of sulphate [7]. Palladium is the most common modifier; the formation of the Pd–Si interelement compound prevents Si either from being lost as the volatile SiO or from forming the refractory SiC [8]. A Pd–Mg matrix modifier allows a maximum pyrolysis temperature of 1400°C but losses as the gaseous monoxide are occasional above 1300°C [7]. Alkali metal fluorides react with silicon to produce metal hexafluorosilicates which are stable at temperatures as high as 1120–1300°C [9]. Formation of silicon carbide is prevented by coating the tube or platform with W, Zr, Ta, La [8,10]; tungsten gave the best results [10]. The effect of the addition of O_2 , CO_2 , CO and H_2 to the purge gas has been investigated [5].

Other techniques

Inductively coupled plasma AES offers a DL of 12 ng ml^{-1} at the most sensitive 251.6 nm line. Ionization effects were reported to be overcome in DCP AES by the addition of lithium buffer [11]. Silicon has a major isotope, ^{28}Si (92%), and two minor isotopes, ^{29}Si (5%) and ^{30}Si (3%), all of which are subject to isobaric overlaps by $^{14}\text{N}_2^+$, $^{15}\text{N}^{14}\text{N}^+$ and $^{15}\text{N}_2^+$. The DL in ICP techniques is controlled by the contamination from the sample introduction system and the plasma torch [12,13]. The addition of tertiary amines was reported to deactivate fluoride, to reduce the blank and to improve the precision [13]. Wavelength dispersive XRF resolves readily the Si peak from those of Al and P but the DL is poor (*ca* $100 \mu\text{g g}^{-1}$) [14]. The importance of fluorimetric [15] and chemilumi-

nescence [16] methods is minimal. Neutron activation analysis is based on the selective $^{29}\text{Si}(\text{n,p})^{29}\text{Al}$ reaction but the overall sensitivity is limited by the low ^{29}Si abundance [14]. The alternative $^{28}\text{Si}(\text{n,p})^{28}\text{Al}$ reaction is interfered with by Al and P.

50.2 ANALYSIS OF REAL SAMPLES

General considerations

Silicon is ubiquitous in the environment and the risk of contamination is particularly acute. Class-100 clean room conditions, polypropylene or PTFE vessels and precleaned Pt crucibles are required [2,7,13]. Disposable syringes or vacutainer tubes are contaminated and should be carefully evaluated prior to clinical analysis [17]. The ICP torch is a common contamination source; the use of a sapphire-tipped torch has been proposed [12,18]. To avoid losses of the volatile SiF_4 closed vessels are used; the addition of excess of H_3BO_3 is recommended to complex free fluoride.

Water

In natural waters Si is present as silicate (dissolved orthosilicic acid) and silica (particulate fraction: biogenic and lithogenic). The spectrophotometric molybdate blue method, usually in automated CF or FIA systems, is standard for silicate [19]. Biogenic silica can be recovered by digestion with NaOH [1,19] and lithogenic silica by the subsequent HF digestion [1]. An alternative speciation scheme is based on the determination of dissolved (direct molybdate blue method), colloidal (molybdate blue method after Na_2CO_3 fusion) and total (ICP AES) silicon [1,2]. Sub-ng amounts of Si have been determined in semiconductor grade water by ICP AES [2] and HR ICP MS [12]. On drying the silicates were reduced with solid LiAlH_4 to silane and then trapped, revolatilized and determined [16].

Biomaterials

In serum and urine Si is determined directly (on dilution) by GF AAS using pyrolytically coated tube and platform atomization, matrix modifier, and background correction with a DL down to 10 ng ml^{-1} [10,17,20,21]. Nitrates of Ca, Mg and La have been compared as matrix modifiers for the analysis of plasma, $\text{Ca}(\text{NO}_3)_2$ was found to be the best [20]. Silicon in bone and soft tissue was determined after acid digestion by GF AAS using wall atomization from a pyrolytic graphite coated tube

and La as matrix modifier with a DL of $\approx 0.1 \mu\text{g g}^{-1}$ [22]. Plasma AES is an alternative [23]. A microwave-assisted digestion procedure has been developed for food and coral soil samples before ICP AES analysis [13]. Biomaterials can be analyzed directly by WD XRF and NAA with a DL of $100 \mu\text{g g}^{-1}$ [14].

Industrial materials

Four methods were compared for the determination of Si in gold [18]. Silicon was determined in gallium arsenide by GF AAS using TaC-coated tube and platform, $\text{Ca}(\text{NO}_3)_2$ matrix modifier and D_2 background correction [24]. Trimethylgallium was decomposed with HCl prior to GF AAS or ICP AES [25,26]. Slurry sampling ZGF AAS was reported to offer a DL of $2\text{--}7 \mu\text{g g}^{-1}$ for the titanium dioxide and zirconium dioxide analysis [27].

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Silver

Silver (Ag, atomic weight 107.87, melting point 961°C , $d = 10.5 \text{ g cm}^{-3}$) is a white, soft lustrous metal. It occurs in the earth's crust with an average abundance of 0.1 ppm, primarily in sulphide ores of Cu, Pb and Zn. The metal dissolves in HNO_3 or in a cyanide solution in the presence of oxygen. Silver exists in solution in the I oxidation state. Alkali metal hydroxides precipitate a dark brown silver oxide, Ag_2O , which dissolves readily in dilute HNO_3 or $\text{NH}_3(\text{aq})$. Chloride and bromide precipitate from neutral or acid solution sparingly soluble, curdy AgCl and AgBr , respectively, which are light sensitive and decompose to Ag^0 . Silver forms stable complexes with iodide, cyanide, thiosulphate and ammonia. Trace analysis for Ag is typically demanded in geology and ecotoxicology.

51.1 SEPARATION AND PRECONCENTRATION

Solvent extraction

Trace quantities of silver can be efficiently extracted as AgI_2^- into MIBK [1] but more often anionic halide [2–6] and thiosulphato [7] silver complexes are extracted with high molecular weight amines or quaternary ammonium salts. Common chelating agents do not interfere [6]. The AgI_2^- complex extracted in the presence of HNO_3 shows poor stability which can be improved by the addition of sulphamic acid or urea [4]. Common chelating extraction reagents include dithizone [8] and dithiocarbamates [9].

Ion exchange

The AgCl_2^- complex is retained by strong anion exchangers [10] whereas it passes unretained through cationites at concentrations below 10 ppm [11]. In samples with higher Ag content most of the Ag is

precipitated as AgCl [11]. Cation exchange separation of Ag^+ has been exhaustively discussed [12]. Sorption of Ag on various chelating resins has been reported [13-16]. The inorganic ion exchanger chromium(III) hexacyanoferrate(III) was found to be a specific sorbent for Ag ions from highly acidic solutions [17]. Silver traces were reported to be separated by electrosorption on a Pt gauze activated by hydrogen [18].

Coprecipitation and other methods

Traces of Ag(I) are reduced to Ag^0 with formic acid [19], hydroquinone [19] or SnCl_2 [11] and can be separated by coprecipitation with Te [13,20,21], Hg [22], Fe and Pd [8] as carriers. Flotation methods for the separation of Ag have been reported [23,24]. Quantitative volatilization of Ag from samples with a complex matrix was obtained at elevated (1200°C) temperatures [25].

51.2 DETERMINATION TECHNIQUES

Spectrophotometry

The most popular is the dithizone method based on the reaction of dithizone with Ag^+ in acid medium (H_2SO_4 , HNO_3 or HClO_4) to form the orange-yellow dithizonate ($\epsilon = 3.05 \times 10^4$ at 463 nm) extractable into CCl_4 . Noble metals are co-extracted with Ag and can be separated by stripping Ag with 1 M HCl. The presence of chloride prevents the formation of Ag dithizonate. More sensitive but less selective is the thio-Michler's ketone method ($\epsilon = 1\text{--}1.4 \times 10^5$). Some macrocyclic compounds have been proposed for extraction-spectrophotometric determination of Ag [26].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of ca $0.05 \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 oxidizing (lean, blue) flame at the most sensitive 328.1 nm line. When multi-element lamps containing Cu are employed, a spectral slit should be used with the 328.1 nm silver line to avoid potential interference from the 327.4 nm Cu resonance line. The determination of Ag by FAAS is interfered with by Cl^- , Br^- , I^- , CrO_4^{2-} , which precipitate Ag ions. Large excess of Al or mineral acids depresses the Ag signal. Platinum and Se do not interfere if a uranium buffer is added [19]. Flame AAS was recommended for the analysis of AgI_2 extracts [4].

Electrothermal atomic absorption spectrometry

Electrothermal AAS offers a DL of 5 pg ml⁻¹ but is plagued by interferences and usually requires matrix modification. Without a modifier a pyrolysis temperature of 650°C could be used that could be increased to 1000°C in the presence of Pd-Mg(NO₃)₂ modifier [27–29]. Other modifiers included NH₄H₂PO₄ [30], (NH₄)₂HPO₄ [31], NH₄NO₃ [32], and Ir [22]. The very small characteristic mass of Ag (ca 1 pg) favours dilution with water as a method for elimination of many interferences. The mechanism of electrothermal atomization of Ag has been discussed [33]. Tellurium, if not completely volatilized, may interfere with GF AAS determination [11].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL in the low ng/ml range at the most sensitive 328.068 nm emission line [9]. The Ag emission tends to be enhanced by the presence of Ca, Cu, Fe, Ni and Co [34]. Especially serious is the overlap by Fe at the 328.130 nm and 328.026 nm lines. Separation of Ag prior to determination is recommended.

Neutron activation analysis

Several radionuclides are formed by the (n,γ) reaction with Ag; the most important is ^{110m}Ag (*t*_{1/2} = 253 d, *E*_γ = 0.68 and 0.88 MeV). Many radionuclides can interfere with a direct γ-spectrum measurement, so a radiochemical separation, usually by ion exchange, is required [10,35].

Mass spectrometry

Silver has two stable isotopes: ¹⁰⁷Ag (51.8%) and ¹⁰⁹Ag (48.2%). The high sensitivity of AAS for Ag has hampered expansion of ICP MS for the determination of this element. Isotope dilution ICP MS has been used for the Ag determination in pure copper; no mass discrimination effect due to the Cu matrix was observed [21].

51.3 ANALYSIS OF REAL SAMPLES

General considerations

Samples and standards should contain 5% HNO₃ to keep Ag in solution. They are sensitive to light and must be stored in amber glass. The presence of Cl⁻ either originating in the sample or introduced as reagents impurity leads to uncontrollable precipitation of AgCl adhering

TABLE 51.1

Determination of silver in water

Water (amount)	Enrichment	Detection	DL (ng/l)	Ref.
Tap (80 ml)	extraction with APDC-DDTC (MIBK)	AAS	300	9
Tap	none	ICP AES	2000	9
Sea (0.9 l)	precipitation with NaBH ₄ with Fe and Pd as carriers	GF AAS	n.g.	37
Sea, CRM river (0.2 l)	sorption of the Ag-dithiophosphoric acid <i>O,O</i> -diethylether complex	GF AAS	0.3	38
Sea (25 ml)	extraction with dithizone (benzene), back-extraction (HNO ₃)	GF AAS	10	8
Natural (2 l)	anion exchange, extraction as AgI ₂ ⁻ (butylacetate)	FAAS	4	39
Sea water (2.5 l)	anion exchange	ID TIMS	<1	40

to the vessel walls and the insoluble residue. Methanol has been used to dissolve any dried TBA⁺-AgBr₂⁻ complex remaining on the glassware [3]. Losses of Ag from solution by adsorption onto borosilicate glass and polyethylene sample containers have been reported [36]. In distilled water over 80% of a 1 ng ml⁻¹ solution may be adsorbed within 11 days; acidification to 0.3 M HNO₃ prevents this process [36].

Water

Filtration through 0.45 µm membranes may bias the dissolved *vs.* suspended ratio of Ag in freshwaters in favour of the latter by adsorption of the dissolved Ag [36]. Coprecipitation [37] or extraction [9,22] followed by GF AAS is the most widely used. The ultratrace determination of Ag in rainwater (10⁻⁶-10⁻⁵ µg ml⁻¹ levels) precluded the use of dithizone extraction for preconcentration because of the high blank. Analytical procedures are summarized in Table 51.1.

Geological materials

Silver is readily collected by lead in fire assay. Cupellation leads to considerable losses and should be avoided. The lead button can be

dissolved in HNO_3 or parted with HClO_4 . Silver is separated either as AgClO_4 precipitated on standing of the perchlorate solution or by reductive precipitation [41]. For lower trace analysis the lead fire assay is not convenient because of high blanks [42]. Silver is effectively collected by Cu fire assay; the button is dissolved in HClO_4 whereupon Ag is precipitated by reduction [19]. Acid attack commonly used for sulphide minerals is hampered by the precipitation of AgCl in the presence of Cl^- . The stability of Ag^+ in HCl media is increased by diethylenetriamine, which reacts with AgCl to form a complex and thus prevents precipitation [3]. Conversion of AgCl into the soluble $\text{Ag}(\text{NH}_3)_2^+$ is not suitable in real sample analysis because the alkaline medium favours precipitation of many matrix components [43]. Another problem related to the acid attack is completeness of leaching of the Ag from the ignited material. In sample roasting, Ag interacts with the rock components to form compounds that are insoluble in *aqua regia* [44]. Silver can be liberated from most samples only after destruction of the silicate matrix by HF or by dissolving the material without thermal pretreatment. Another decomposition technique is KClO_3 – HCl attack. In order to decrease the temperature of the KClO_3 decomposition and to avoid formation of perchlorates, MnO_2 was added as a catalyst [42]. Silver can be determined in rocks and ores directly after sample decomposition by FAAS [45] and GF AAS [34,46] with a DL of 2 and 0.01–0.1 $\mu\text{g g}^{-1}$, respectively. Combined methods for the determination of silver in geological samples are summarized in Table 51.2.

Biological materials

Biological materials are usually analyzed by GF AAS. Plasma, blood and urine are analyzed directly after dilution with Triton X-100 with a DL of 0.1–1 ng ml^{-1} [28,30,32]. For urine the DL can be decreased to 0.03 ng ml^{-1} by extraction prior to GF AAS [6]. Silver is tightly bound to protein and the signal is smaller than that from an aqueous standard. Silver-spiked plasma [30,50] and silver proteinate solution [30] have been recommended for calibration. Tissues (soft and hard) are analyzed by GF AAS after acid digestion with DLs down to sub-ng/g. Digestion with HNO_3 is recommended for tissue samples especially if a further ion exchange or extraction enrichment step is involved [30,32]. The determination of Ag by NAA on lead fire assay was reported to give elevated results [51].

TABLE 51.2

Determination of silver in geological materials

Material (amount)	Sample decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Rock, ore (20–50 g)	NiS fire assay, the bead dissolved in HCl	copptn. with Te	RNAA	2.5 ^a	47
Ores	Cu fire assay	pptn. with hydroquinine or formic acid	AAS	n.g.	19
Pt ores	roasting, lead fire assay, dissoln in HClO ₄ –AcOH	pptn. with formic acid	FAAS	n.g.	41
CRMs (0.5 g)	HCl–HNO ₃	copptn. with Hg	GF AAS	n.g.	22
Ores (1 g)	HNO ₃ or HNO ₃ – H ₂ SO ₄	extrn. with <i>o</i> - iodoformazan (CH ₂ Cl ₂)	DCP AES	50	34
Ores (0.1–1 g)	KClO ₃ –HCl	extrn. with TPP	FAAS	0.05	42
Ores (1 g)	HCl–HClO ₄ – H ₂ SO ₄ , HF	extrn. as AgI ₂ (MIBK), stripping with HNO ₃ –HCl	FAAS	0.02	1
CRMs (0.5 g)	<i>aqua regia</i> – HClO ₄ –HF	none	GF AAS	0.01	31
Rocks	<i>aqua regia</i>	copptn. with Te	GF AAS	1–2 ^a	20
Rocks (5 g), ores (2 g)	<i>aqua regia</i> –HF, the residue fused with Na ₂ O ₂	cation exchange	GF AAS	n.g.	11
Soils, rocks, sediments (2 g)	<i>aqua regia</i>	extrn. of AgI ₂ with TOMA into MIBK	FAAS	0.01	4
Cu ore, brass (1 g)	HNO ₃	sorption on chelate resin	FAAS	n.g.	15
Ores (≤ 1 g)	Br ₂ , HNO ₃ , HF	extrn. of AgBr ₂ [–] with TBA	FAAS	0.01	3

Material (amount)	Sample decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Soils, sediments, rocks (2 g)	<i>aqua regia</i> - Br_2	extrn. of AgI_2^- with TOMA (MIBK)	FAAS	0.10	5
Soils (0.5 g)	fusion with $\text{K}_2\text{S}_2\text{O}_7$	extrn. as AgCl_2^- with Aliquat-336 (MIBK)	FAAS	0.1	2
CRM soil (0.2 g)	HCl-HNO_3	sorption of the Ag- dithiophosphoric acid <i>O,O</i> -diethyl ester complex on carbon	GF AAS	n.g.	38
Pt ore (0.5 g)	fusion with LiBO_2 , dissoln. in HNO_3	SPE on polyDDTC resin, then dissolved in 50% H_2O_2	ICP AES	0.14	13
CRMs (0.5 g)	fusion with Scintex Geoflux	extrn. with APDC (MIBK)	GF AAS	n.g.	48
CRMs, coal and rock	fusion with NaOH and Na_2O_2	anion exchange	NAA	$1-10^a$	35
Rock (0.5 g)	fusion with Na_2O_2 , lead fire assay	lead button fused with NaOH - Na_2O_2	NAA	$1-10^a$	49
Copper ore (50 mg)	none	volatilization with addition of Florisil- CaO	FAAS	n.g.	25

^a In the sample, ng/g.

Industrial materials

Acid dissolution with HNO_3 [3,21], *aqua regia* [47] and other oxidizing mixtures [3,41,52] followed by the decomposition of the residue by fusion [11], if necessary, is the most popular approach. The use of microwave wet digestion is recommended [52]. Analytical procedures are summarized in Table 51.3.

TABLE 51.3

Determination of silver in industrial materials

Material (amount)	Sample decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Concentrates, mattes (2 g)	dissoln. in <i>aqua regia</i> -HF, the residue fused with Na_2O_2	cation exchange	GF AAS	n.g.	11
Concentrates	roasting, lead fire assay, dissoln. in HClO_4 -AcOH	pptn. with formic acid	FAAS	n.g.	41
Concentrates (1 g)	HCl - HClO_4 - H_2SO_4 , HF	extrn. of AgI_2^- (MIBK), stripping with HNO_3 -HCl	FAAS	0.02	1
Concentrates, electrolytic precipitate	roasting, lead fire assay, dissoln. in HClO_4 -AcOH	pptn. with formic acid	FAAS	1	41
Concentrates (≤ 1 g)	Br_2 , HNO_3 , HF	extrn. of AgBr_2^- with TBA (CHCl_3), stripping with HBr	FAAS	0.01	3
Concentrates, refinery borax slag, sweeps	copper fire assay	pptn. with hydroquinone or formic acid	AAS	n.g.	19
Electrolytic Cu metal (0.5-1 g)	HNO_3	electrosorption on hydrogen activated Pt gauze	FAAS; VIS	1 ^a	18
Cu metal and alloys (≤ 1 g)	HNO_3	extrn. of AgBr_2^- with TBA (CHCl_3), stripping with HBr	FAAS	0.01	3
Pure Cu metal (1 g)	HNO_3	copptn. with Te	ID ICP MS	0.02	40
Copper tailings (50 mg)	volatilization with addition of Florisil-CaO	none	FAAS	n.g.	25
Ore dressing products (0.1-1 g)	KClO_3 -HCl	extrn. with TPP	FAAS	0.05	42
Zinc process solutions (≤ 75 ml)		extrn. of AgBr_2^- with TBA into CHCl_3 , stripping with HBr	FAAS	0.01	3

DPTU, *N,N'*-diphenylthiourea; ^a absolute detection limit, μg .

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Sodium and potassium

Sodium (Na, atomic weight 22.99, melting point 98°C, $d = 0.97 \text{ g cm}^{-3}$) and potassium (K, atomic weight 39.10, melting point 64°C, $d 0.86 \text{ g cm}^{-3}$) are among the most abundant elements in the earth's crust and seawater. They are soft, silvery metals which are readily oxidized on exposure to air to form a mixture of hydroxide and carbonate. Both metals dissolve vigorously in water and lower alcohols releasing hydrogen. Sodium and potassium form monovalent cations. Because of the large abundance of Na and K the need for their trace determination is restricted to ultrapure materials and biological tissues, especially if little sample is available.

52.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Crown ethers of the 12-crown-4 [1] and 15-crown-5 [2] type are fairly selective extractants for Na^+ whereas K^+ is most strongly complexed by 18-crown-6-type compounds [2–6].

Spectrophotometry

Highly selective methods for Na [1,6,7] and K [3–5] are based on the extraction of their complexes with crown ethers, often paired with a chromogenic anion [1,5]. The elements can be determined simultaneously after separation in an FI system [6].

Atomic absorption spectrometry

Flame AAS uses typically an air- C_2H_2 , oxidizing (lean, blue) flame albeit an H_2 -air flame has been proposed [8]. The most intensive Na

line at 589.0 nm ($0.005\text{--}0.01\text{ }\mu\text{g ml}^{-1}$) is actually a doublet at 589.0 and 589.6 nm. The most sensitive K line is at 766.5 nm. A sensitivity of $0.02\text{--}0.04\text{ }\mu\text{g ml}^{-1}$ is obtained either with an EDL or HCL. A red filter absorbing radiation below 650 nm should be used. Ionization of Na and K should be controlled by the addition of Cs or La. In the case of Na, KCl can be used as the ionization buffer. Flame AAS can be used in combination with slurry sampling [9] or FI [10]. Graphite furnace AAS shows a characteristic mass of 1 pg both for Na and K. A molybdenum tube atomizer and thiourea as a matrix modifier have been proposed for the determination of K [11].

Atomic emission spectrometry

Sodium and potassium give an intense emission in air- C_2H_2 flame at 589.0 and 766.49 nm, respectively. Surface-active 18-crown-6 derivatives were found to enhance the flame emission [12]. Slurry sampling has been employed [9]. Laser-induced ionization in flames was reported for K [13]. Graphite furnace AES has been used for the determination of Na and K with a DL of 0.5 pg [14,15]. Inductively coupled plasma offers a DL of $10\text{--}20\text{ ng ml}^{-1}$ for Na and an order of magnitude poorer for K at the above-mentioned lines.

Mass spectrometry

Potassium has three stable isotopes: ^{39}K (93.26%), ^{40}K (0.01%) and ^{41}K (6.73%) whereas Na is monoisotopic ^{23}Na . Thermal ionization MS is used for the determination of K [16].

Neutron activation analysis

Neutron activation analysis for Na is based on the reaction $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$ and counting the ^{24}Na nuclide ($t_{1/2} = 15\text{ h}$, $E_\gamma = 1.37$ and 2.75 MeV). The higher energy peak is preferred for INAA as it is virtually interference free, except when high excess of Al is present. The determination of K is based on the $^{41}\text{K}(n,\gamma)^{42}\text{K}$ reaction and counting the ^{42}K nuclide ($t_{1/2} = 12.8\text{ h}$, $E_\gamma = 1.53\text{ MeV}$). Radiochemical separation from Na was necessary.

52.2 ANALYSIS OF REAL SAMPLES

The determination of Na and K in biological samples has been reviewed [17,18]. In ultratrace analysis, significant contamination is

possible, especially from water [13]. Effects of needle size and storage temperature on the measurement of K in serum has been discussed [19]. Flame AES is the recommended technique for routine analysis of clinical samples. An automated flame photometer has been described [20]. *On-line* dialysis was used to avoid interferences and blocking of the fine jet of the atomizer in FI FAES analysis of blood serum [21]. Sodium and potassium in serum have been determined by spectrophotometry [1,7] and FI ICP AES [22]. Potassium in cerebrospinal fluid was determined directly by FI FAAS; the physiological level of Na was included in the standards to compensate for the Na content [23]. Graphite furnace AAS was recommended for sub-nanolitre biofluid samples [24]. X-ray (ED XRF) microanalysis of liver mitochondria has been used [25]. Simultaneous determination of Na and K inside single human erythrocytes was accomplished by LE AES with a DL down to 8 fg [26]. Sodium and potassium were determined in single erythrocytes by CZE with fluorescence detection at sub-femtomolar levels [27].

Foodstuffs are analyzed as slurries, directly [9] or after dry ashing [28], or on microwave-assisted digestion with a mixture of HNO_3 – H_2SO_4 – H_2O_2 [29,30]. Fusion with molten NaOH – NaNO_3 in an open system has been proposed for decomposition of leaf samples prior to potassium determination [32]. An FI system incorporating a dialysis unit has been used for the FAES determination of K in wines [33]. Determination of K in plant samples after microwave assisted acid decomposition and FI extraction with cryptand[2.2.2] has been reported [31].

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Strontium

Strontium (Sr, atomic weight 87.62, melting point 770°C, $d = 2.6 \text{ g cm}^{-3}$) is silvery white, fairly soft metal. It occurs in the earth's crust with an average abundance of 380 ppm, primarily as celestite (SrSO_4) and strontianite (SrCO_3). The biologically hazardous ^{90}Sr nuclide exists in the environment as a result of atmospheric nuclear weapon testing, nuclear waste discharge and nuclear accidents. Strontium reacts readily with water or oxygen to form the hydroxide or oxide. The aqueous chemistry of strontium is almost entirely that of the Sr^{2+} ion. Strontium oxide dissolves in water to give an $\text{Sr}(\text{OH})_2$ solution. The insoluble Sr salts include carbonate, fluoride, oxalate and sulphate. Strontium forms weak complexes with O-donor ligands.

53.1 SEPARATION AND PRECONCENTRATION

Coprecipitation

Strontium can be separated from Ca by precipitating SrSO_4 from an EDTA solution (pH 5) or by precipitating calcium as $\text{Ca}(\text{OH})_2$ with dilute NaOH. The most popular separation of Sr from Ca is based on the selective leaching of Ca with dilute or concentrated HNO_3 on precipitation of carbonates [1,2]. Strontium can also be coprecipitated with the Ca carrier as the oxalate [3]. The bulk of Ca can be removed by precipitation under slightly different conditions [4]. Traces of Sr can be precipitated as SrCrO_4 with Ba as carrier.

Extraction

Strontium can be extracted as its complex with 8-hydroxyquinoline into CHCl_3 [5,6], 18-crown-6 ethers [7,8] or dicarbollides (in the pres-

ence of EDTA and polyethylene glycols) [9,10]. Ion exchange [4] and extraction chromatography of the substituted 18-crown-6 ether strontium complexes are also used, especially for the purification of ^{90}Sr in radiochemical procedures [3,6].

53.2 DETERMINATION TECHNIQUES

Atomic absorption spectrometry

Flame AAS offers a sensitivity of 0.1 mg l^{-1} in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$, reducing (rich, red) flame at the 460.7 nm line. An alkali metal salt should be added to control ionization [11]. Chemical interferences (Al, P, Si and Ti), which occur in the air- C_2H_2 flame, should be controlled by the addition of 1% of LaCl_3 [12] or catechol and pyrogallol [13]. These interferences are efficiently removed in the $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame [11]. A systematic study of the Al interference has been presented [14,15]. Graphite furnace AAS shows a characteristic mass of 1.4 pg using atomization from a pyrocoated tube wall [16]. Mechanisms of the electrothermal atomization of Sr have been comprehensively discussed [17].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers sub-ng/ml DLs at the most sensitive 407.77 and 421.55 nm lines which are virtually free from spectral interferences [18,19]. Emission of Sr in $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame at the 460.7 nm line is sufficiently strong to allow practical applications [8].

Mass spectrometry

Strontium has four stable isotopes: ^{84}Sr (0.55%), ^{86}Sr (9.86%), ^{87}Sr (7.0%) and ^{88}Sr (82.58%) and thus it is readily amenable to TI MS. The ^{85}Rb can be monitored to detect whether any correction is required for the ^{87}Rb interference on the ^{87}Sr peak. Mass fractionation effects are corrected by normalizing all data to the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Inductively coupled plasma MS offers DLs of $10\text{--}30 \text{ pg ml}^{-1}$ [5,20] but suffers (in addition to ^{87}Rb) from isotopic overlaps with ^{84}Kr and ^{86}Kr (Ar gas impurities) which must be corrected by blank subtraction. No interferences from polyatomic ions were reported [5]. The ^{88}Sr nuclide free from isobaric interferences is counted [5,20]. ^{86}Sr is used as the spike in ID ICP MS [20]. Precision is considerably improved by using ^{115}In as an internal standard [5]. A double focusing magnetic sector mass analyzer after ICP has been used for a high-precision determination of Sr isotopic ratios [21].

Nuclear methods

^{90}Sr can be determined by β -spectrometry after separation from other β -emitters [2]. Since ^{90}Sr ($t_{1/2} = 28.8$ y) is in secular equilibrium with ^{90}Y ($t_{1/2} = 64.1$ h) the latter is often separated and counted instead in order to derive the Sr concentration [22]. Irradiation of ^{90}Sr produces the short-lived ^{90}Y which is separated and counted [23]. Stable Sr nuclides are determined using the reactions $^{84}\text{Sr}(n,\gamma)^{85\text{m}}\text{Sr}$ and $^{86}\text{Sr}(n,\gamma)^{87\text{m}}\text{Sr}$. Of the produced nuclides: $^{85\text{m}}\text{Sr}$ ($t_{1/2} = 70$ min, $E_\gamma = 0.233$ MeV) and $^{87\text{m}}\text{Sr}$ ($t_{1/2} = 2.8$ h, $E_\gamma = 0.388$ MeV) the latter offers a better sensitivity and is chosen. In many cases a radiochemical separation is needed prior to γ -ray spectrometry [5,6].

Other methods

Strontium reacts with the bisazo derivatives of chromotropic acid of which Nitroanthanilic S is particularly suitable. Selectivity is, however, poor. Energy-dispersive XRF has been evaluated for Sr determination [24].

53.3 ANALYSIS OF REAL SAMPLES

The primary interest focuses on the ^{90}Sr of which determination by various radiochemical and MS techniques has been compared [25]. ICP AES is the primary technique for stable Sr in clinical [18] and environmental materials [19]. The concentration in human serum has been determined by ICP MS and NAA [5,6] and GF AAS [16]. Recovery of Sr from river sediment has been studied in detail [12].

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Tantalum

Tantalum (Ta, atomic weight 180.95, melting point 2996°C, $d = 16.6 \text{ g cm}^{-3}$) is a grey, hard malleable metal. It occurs in the earth's crust with an average abundance of 1 ppm, primarily in columbite–tantalite. The metal is dissolved in HF (with the formation of TaF_7^{2-}) and in fused alkalis to produce TaO_4^{3-} . The most stable oxidation state is V. In the absence of complexing agents Ta(V) hydrolyzes over the pH range 0–14 with possible formation of a variety of polymerized forms which give pseudosolutions or fall out as a white precipitate. Tantalum forms oxalate, tartrate, fluoride and peroxide complexes. Analytical solution chemistry of Ta is difficult because complexing agents that are required to keep Ta in solution may affect many of its chemical reactions. The primary need for trace Ta determination exists for geological materials.

54.1 SEPARATION AND PRECONCENTRATION

Coprecipitation

During the heating of acid solutions free of complexing agents Ta hydrolyzes and coagulates to form hydrous oxides that are readily collected by Zr(OH)_4 , Fe(OH)_3 and Mg(OH)_2 in acidic, neutral and alkaline solutions, respectively. Ta can be precipitated from solutions containing not too much oxalate, tartrate or EDTA with cupferron [1].

Extraction

Extraction of the stable Ta fluoride complexes into oxygen-containing solvents is a convenient method for the separation of Ta from Ti, Zr, Sn, Mo, U, W and Fe and, by a careful optimization of the extraction conditions, also from Nb [2]. Tantalum can be stripped from the organic

phase with H_2O_2 . Extraction from oxalate and fluoride containing solution with *N*-benzoyl-*N*-phenylhydroxylamine into CHCl_3 or toluene is used for the separation of Ta (Nb, Mo and W are co-extracted) [3–5]. Extraction of Ta with various hydroxamic acids has been discussed [3].

Chromatographic methods

Many anion-exchange procedures involve separation of Ta as the fluoride complex. The TaF_6^- can be retained on polyurethane foams [6]. Reversed-phase HPLC determination as 5-Br-PADAP complex from tartrate media has been reported [7].

54.2 DETERMINATION

Alkaline or acidic fusion [1,4] and acid attack with HF-containing mixtures [5,7,8] are alternatively used for sample decomposition. When an alkaline melt is leached with water, Ta remains in the solid phase while W, Mo, V and Re (but not Nb) pass into the aqueous solution. Some fluxes, e.g. $\text{K}_2\text{B}_4\text{O}_7$ were reported to be contaminated with Ta [1]. Trace levels of Ta are neither essential nor toxic so there is almost no work related to the analysis of biomaterials [9]. Tantalum occurs in seawater as $\text{Ta}(\text{OH})_5$ [9]. The predominant technique to determine Ta in rock samples is INAA. Spectrophotometry is still widely used in many laboratories whereas other techniques have only minor (ICP AES, ICP MS) or no (AAS) importance for trace analysis. Analytical methods for the determination of Ta in real samples are summarized in Table 54.1.

Spectrophotometry and fluorometry

In dilute HF medium Ta forms an anionic complex TaF_6^- which combines with the basic dye Methyl Violet to form an ion pair extracted with benzene ($\epsilon = 7.5 \times 10^4$ at 605 nm) [2]. Moderate amounts of many elements including Nb, Ti, Zr, Hf and W do not interfere. Rhenium interferes seriously while Mo and Al interfere by changing the fluoride concentration. Fluorescence of Ta chelates with morin and quercetin in acid micellar media (CTA) was reported to offer DLs in the 0.03–0.05 ppm range [10].

Neutron activation analysis

The irradiation of ^{181}Ta gives rise to the metastable $^{182\text{m}}\text{Ta}$ ($t_{1/2} = 16.5$

TABLE 54.1

Analytical procedures for the determination of Ta

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. with HCl-HF	copptn. with cupferron	ICP MS	0.02	1
GeoCRMs (0.1–1 g)	HNO_3 , HF (microwave assisted)	extrn. with BPHA (CHCl_3)	ICP MS	0.08 ^a	5
GeoCRMs	fusion with Na_2CO_3	extrn. as TaF_6^- (MIBK)	VIS	1	2
CRMs rocks, soils, sediments (0.5–1 g)	not given	sorption as TaF_6^- on polyurethane foam	RNAA	100 ^b	6
GeoCRMs (0.5 g)	HF-HClO_4 , HCl	RP HPLC as 5-Br- PADAP complex	VIS	2 ^a	7
GeoCRMs (0.1 g)	HNO_3 -HF	matrix removal as SiF_4	ICP MS	0.04	8

^a In the solution fed, ng/ml; ^b absolute detection limit, ng.

min) and the long-lived ^{182}Ta ($t_{1/2} = 111$ d). The latter gives a characteristic double γ -peak which is usually counted after a long decay necessary to reduce the background from major and rare earth elements. An ADL of ca 20 ng is common [6,11].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 20–30 ng ml⁻¹ at the most sensitive (226.14, 263.56, 240.06 nm) lines. Spectral lines and coincidences have been comprehensively discussed [12]. Interferences are common so the separation of Ta from the matrix is recommended [1].

Inductively coupled plasma mass spectrometry

Tantalum has two naturally occurring isotopes ^{181}Ta (99.99%) and ^{180}Ta (0.01%, $t_{1/2} > 10^{12}$ y). The high-resolution mode was employed in the determination of low levels ($<0.5 \mu\text{g g}^{-1}$) of Ta in the presence of high

levels of W, in order to negate the interference by $^{182}\text{W}^+$ due to the tailing to the low mass side [1]. Internal standarization with Re has been used to compensate for the matrix suppression with U [1].

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Technetium

Technetium (Tc, atomic weight 98.9, melting point 2172°C, $d = 11.5 \text{ g cm}^{-3}$) is an artificial element produced in relatively large amounts in nuclear fission and released into the environment from nuclear power plant effluents, nuclear weapons testing and nuclear medicine. Very small amounts of Tc in nature may be due to spontaneous fission of ^{235}U . Technetium dissolves in oxidizing acids (HNO_3 , H_2SO_4), Br_2 -water and H_2O_2 to form the strong pertechnetic acid, HTcO_4 . Pertechnate is very stable in aqueous solution and, unlike permanganate, is only a weak oxidant. Technetium occurs in the V and VII oxidation states, the latter being much more stable. The need for the trace Tc determination is due to the radiological relevance of Tc to health and the utilization of ^{99}Tc as a tracer in marine chemistry [1]. The only environmentally relevant nuclide is ^{99}Tc , a β -emitter of low energy and a long half-life ($t_{1/2} = 2.13 \times 10^5 \text{ y}$). Determination of ^{99}Tc in natural samples has been reviewed [1,2].

55.1 SEPARATION AND PRECONCENTRATION

Extraction

Extraction of TcO_4^- with tri-*n*-octylamine [3–5], tri-*iso*-octylamine [4,6,7] or TBP [5–7] into nonpolar solvents is commonly used, often in series, for the radiochemical purification of ^{99}Tc (especially from Ru). Alternatively, Ru can be extracted into CCl_4 in the presence of NaOCl at pH 4 leaving TcO_4^- in solution [6]. Extraction of Tc with dithiocarbamates has been reported [8,9].

Coprecipitation

Coprecipitation of ^{99}Tc as Tc_2O_7 [10] or Tc_2S_7 [11–13] with Re(VII) [10–12] or Cu(II) [13] as carrier has been developed. Technetium is also coprecipitated as an ion pair of TcO_4^- with Ph_4As^+ with the bulk of the salt [12]. Reductive coprecipitation of Tc with Fe(OH)_2 in the presence of $\text{K}_2\text{S}_2\text{O}_5$ has been proposed [14]. Electrodeposition of Tc is the end step of β -counting methods [2,10,15].

Other techniques

Sorption of Tc has been widely discussed [16,17]. The most popular is retention of TcO_4^- by anion exchange and stripping with 6–14 M HNO_3 [4,6,10,11,18–20]. Volatilization of Tc from soil in a stream of O_2 has been reported [21]. Removal of matrix Ru by volatilization of RuO_4 from hot H_2SO_4 solution is an alternative [3,6,12,18] (*cf.* Chapter 47).

55.2 DETERMINATION TECHNIQUES

β -Spectrometry

β -Spectrometry is based on the counting of ^{99}Tc by liquid scintillation. Specific activity is 0.64 Bq ng^{-1} ($E_\gamma = 293 \text{ keV}$). Technetium must be isolated from the interfering nuclides and the sample matrix. The usual ADL is 1–15 pg [1].

Mass spectrometry

Mass spectrometry suffers from the isobaric overlap by ^{99}Ru (which accounts for 12.7% of natural Ru). This can be corrected at $m/z = 101$ considering the known isotopic abundances of ^{99}Ru and ^{101}Ru [1]. Thermal ionization MS offers an ADL down to 1 fg [22–24]. The negative ionization mode was proposed to alleviate the isobaric interferences. A disadvantage is that the only available spikes, ^{98}Tc and ^{97}Tc , form ions with ^{17}O and ^{18}O at the $^{99}\text{TcO}_4^-$ position [23]. Ionization of Tc can be enhanced by the addition of La_2O_3 and $\text{Ca(NO}_3)_2$ [23]. Resonance ionization MS has discussed [22]. Inductively coupled plasma MS offers a DL of 0.6 pg ml^{-1} [25] which decreases to 0.1 pg ml^{-1} for HR ICP MS and to *ca* 3 fg ml^{-1} for HR ICP MS with ultrasonic nebulization [6,26]. As well as ^{99}Ru , the ions MoH^+ , Zn , NiCl^+ , CoAr^+ and doubly charged Hg and Pt may interfere [27]. Technetium forms several polyatomic ions and shows a pronounced memory effect [28].

Other techniques

Spectrophotometry lacks sensitivity although a UV detection for a HPLC effluent was able to cope with as little as 0.5 ng TcO_4^- [29]. The use of AAS has been discussed [30]. Although absorption lines from other elements can be used, laboratory fabricated lamps are required for a good sensitivity. In FAAS the air- C_2H_2 reducing (rich, yellow) flame offers a sensitivity of $3 \mu\text{g ml}^{-1}$ at 261.4 nm. The following ICP emission lines were recommended: 254.324 nm (DL 4 ng ml^{-1}), 261.000 nm (DL 4.4 ng ml^{-1}) and 264.702 (DL 4.5 ng ml^{-1}) [25,31]. Use of FANES has been reported [32]. Determination of ^{99}Tc by NAA offers an ADL of 2–3 pg [1,33]. Analytical techniques for the determination of Tc have been reviewed [22].

55.3 ANALYSIS OF REAL SAMPLES

The environmental levels of ^{99}Tc and the emitted β -energy are very low so a separation–preconcentration step is required. It usually involves an enrichment by anion exchange or coprecipitation, followed by decontamination (especially from Ru [26]) by extraction. The recovery of Tc is measured by γ -counting of the $^{95\text{m}}\text{Tc}$ tracer and is usually 50–60% [6,14,21,34,35]. At environmentally relevant levels the Tc β -radiation is absorbed by laboratory glassware so no special precautions are required (unless the sample itself is radioactive). Determination of Tc in nuclear samples has been discussed [28].

Water

Analytical methods for the determination of Tc are summarized in Table 55.1. Anion exchange is the most widely used preconcentration technique, especially if a sample of 200–500 l is required. The natural oxygen present in seawater is sufficient to ensure the presence of TcO_4^- and addition of oxidizing agents (e.g. H_2O_2 [3]) is not necessary [4].

Sediment, soil and biota

Dry ashing [3,6,18,21] or calcination [2,10] followed by the dissolution of the residue in HNO_3 is the usual choice. The volatility of Tc_2O_7 raises the possibility of Tc loss during ashing which must be carefully controlled. Since Tc is not incorporated in the matrix it can be successfully leached with hot concentrated HNO_3 . Analytical methods for the determination of Tc in solid environmental samples are summarized in Table 55.2.

TABLE 55.1

Analytical methods for the determination of Tc in water

Water (amount)	Separation/ preconcentration	Detection	DL (pg/l)	Ref.
Sea, rain (5–30 l)	anion exchange, volatilization of Ru	ICP MS		6, 18
Sea (200–400 l)	anion exchange, volatilization of Ru, extraction with T- <i>i</i> -OA (xylene)	β -spec		3
Sea (50 l)	anion exchange, coprecipitation as Tc ₂ S ₇ with Re(VII)	RNAA		11
Sea (500 l)	anion exchange, SPE of the resin with TOA (xylene), coprecipitation of Tc as Tc ₂ S ₇ with Cu(II)	β -spec		13
Sea	reductive coprecipitation with Fe(OH) ₂ ; extraction of TcO ₄ ⁻ (MEK), cation and anion exchange	ICP MS		14
Sea (25 l)	reductive coprecipitation with Fe(II); extraction with TBP (xylene), back extraction (NaOH), extraction as TcO ₄ ⁻ (MEK) evapn.	ICP MS	6	27
Natural (500 l)	anion exchange, extraction of TcO ₄ ⁻ with T- <i>i</i> -OA (xylene), electrodeposition	β -spec	0.005	4
Natural (300 l)	coprecipitation as Tc ₂ O ₇ with Re(VII), extraction of TcO ₄ ⁻ (MIBK), anion exchange, electrodeposition	β -spec	0.075	10
Waste (50 ml)	anion exchange	β -spec	7500	19

MEK = methylethyl ketone.

Speciation

Speciation of Tc complexes is important in radiopharmaceuticals (e.g. skeletal imaging agents), biomaterials and waste. Technetium species have been separated by anion exchange, size-exclusion and reversed-phase chromatography and detected by spectrophotometry and radiometry [29,30].

TABLE 55.2

Determination of Tc in soil sediment and biota

Sample (amount)	Decomposition	Separation/pre-concentration	Detection	DL (pg/g)	Ref.
Soil	leaching with HNO_3	pptn. with $\text{Fe}(\text{OH})_3$, extrn. of TcO_4^- (TBP), back-extrn. NaOH , anion exchange, extrn. of TcO_4^- (cyclohexanone), back extrn. ($\text{CCl}_4\text{--H}_2\text{O}$)	ICP MS	0.003 ^a	21
Soil (50 g ash)	dry ashing	volatn. of Tc with O_2 , collected in K_2CO_3 soln., extrn. of TcO_4^- (cyclohexanone), back-extrn. ($\text{CCl}_4\text{--H}_2\text{O}$)	ICP MS	0.5 ^a	35
Soil (0.25 g)	fusion with Na_2O_2 , dissoln. in HNO_3	<i>on-line</i> sorption	ICP MS	20	36
Soil		anion exchange, extrn. with T- <i>i</i> -OA, TBP (cyclohexanone)	ICP MS	1.1 ^a	7
Soil		anion exchange, extraction of TcO_4^- (cyclohexane)	ICP MS	0.003 ^a	34
Soil, sediment (<50 g)	dry ashing, dissoln. in $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2\text{--K}_2\text{S}_2\text{O}_8$	extrn. with TBP (xylene), back-extrn. NaOH , extrn. MEK , evapn.	ICP MS	0.003	27
Soils, sediments (10–20 g)	dry ashing	volatn. of Ru, anion exchange	ICP MS	n.g.	6
Soils, biota (200 g dry)	calcination, dissoln. in HNO_3	copptn. as Tc_2O_7 with Re, extrn. of TcO_4^- (MIBK), anion exchange, electrodeposition		0.1	10

continued

TABLE 55.2 (continuation)

Sample (amount)	Decomposition	Separation/pre- concentration	Detection	DL (pg/g)	Ref.
Soils, vegetables	HNO ₃ – H ₂ SO ₄ – H ₃ PO ₄	removal of Ru, pptn. as Tc ₂ S ₇ with Re carrier, copptn. with TPA	β-spec	n.g.	12
Sediment (5–10 g)	dry ashing	anion exchange, extrn. of TcO ₄ [–] (cyclohexanone)	MS	n.g.	20
Sediments, algae	calcination, dissoln. in H ₂ SO ₄	extrn. of TcO ₄ [–] with TBP (xylene), back- extrn. into NaOH, electrodeposition	β-spec	n.g.	2
Sediments, biota (20 g), milk (1 l)	dry ashing	anion exchange, pptn. as Tc ₂ S ₇ with Re carrier	RNAA	n.g.	11
Algae (1–30 g)	leaching with 9 M HNO ₃	volatn. of Ru, anion exchange	ICP MS	n.g.	6 18
Algae	HNO ₃	extrn. with TOA (xylene); copptn. as Tc ₂ S ₇ with Cu(II)	β-spec	n.g.	13
Seaweed (10–20 g)	HNO ₃	anion exchange, volatn. of Ru, extrn. with T- <i>i</i> -OA (xylene)	β-spec	n.g.	3
Nuclear waste	dry ashing, fusion with K ₂ CO ₃	extrn. as TcO ₄ [–] (MEK)		n.g.	37

^a In the solution fed, pg/ml.

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Tellurium

Tellurium (Te, atomic weight 127.6, melting point 450°C, $d = 6.24 \text{ g cm}^{-3}$) is a metalloid which exists in two allotropic forms: amorphous black powder and silver–white shiny crystals. It occurs in the earth's crust with an average abundance of 0.01 ppm, primarily in pyrite ores. Tellurium dissolves in dilute HNO_3 to give tellurous acid, H_2TeO_3 , in oleum to give a red solution of Te_4^{2+} and in a polysulphide solution to form tetrathiotellurate, TeS_4^{2-} . The element is commonly found in oxidation states -II, IV and VI, Te(IV) being the most stable. The amphoteric Te(IV) is precipitated by $\text{NH}_3(\text{aq})$ and alkalis. Elemental Te is precipitated from acidic or ammonia TeO_3^{2-} solutions by SO_2 , SnCl_2 and NH_2OH or N_2H_4 , respectively. Strong oxidants (e.g., MnO_4^-) oxidize tellurite (TeO_3^{2-}) to tellurate (TeO_4^{2-}). The need for trace analysis for Te results from occupational exposure concerns (Te compounds are toxic) and its applications in electronics and metallurgy (microalloying).

56.1 SEPARATION AND PRECONCENTRATION

Volatilization

Tellurium hydride TeH_2 is obtained in acidic media by reduction of Te(IV) with NaBH_4 . To form the hydride Te(VI) must be reduced to Te(IV), usually by boiling with HCl [1–3]. The hydride formation is interfered by transition metals, e.g. Cu and Ni, and hydride-forming elements (As, Bi, Se, Sn and Pb) [2,4–6]. Iron(III) was reported to alleviate the Cu and Ni interference [4]. Lead matrix was removed by precipitation [5]. Tellurium hydride was preconcentrated by trapping in a graphite furnace at 150–500°C [1,3]. Formation of a volatile Te compound by reaction with (4-fluorophenyl)magnesium bromide has been reported [7].

Extraction

Extraction of Te(IV) from concentrated HCl with MIBK has been proposed [8]. Elements forming oxychlorocomplexes (Fe(III), Cr(VI), Sn(IV)) should be removed, e.g. by extraction from an HCl medium into ethylacetate, after oxidation of Te(IV) to Te(VI) with $\text{Cr}_2\text{O}_7^{2-}$. Tellurium was separated from excess of Cu, Fe(III), Pb and Zn by extraction of its xanthate complex from 9.5 M HCl into cyclohexane in the presence of thiosemicarbazide to mask Cu [9]. Tellurium can be stripped from the extract with 16 M HNO_3 [9]. For samples rich in Cu the preliminary separation of Te by coprecipitation with $\text{Fe}_2\text{O}_3(\text{aq})$ is necessary [9]. Co-extraction of As is avoided by AsBr_3 during the decomposition step [9]. Extraction of the Te-bis(trifluoroethyl)dithiocarbamate complex into toluene has been reported [7].

Coprecipitation

Coprecipitation of Te(IV) with $\text{Fe}(\text{OH})_3$ at pH 8–9 (followed by flotation) [10] and with $\text{Mg}(\text{OH})_2$ [3] has been reported. Elemental Te was coprecipitated with As and Pd as collector on reduction with hypophosphorous acid [5] and ascorbic acid [11], respectively.

Cation exchange

Cation exchange has been applied to the separation of Te(VI) (anionic) and Te(IV) (retained as $\text{TeO}(\text{OH})^+$ or $\text{Te}(\text{OH})_3^+$) complexes [12,13]. Cation exchange separation was used to retain the interfering Cu, Hg, Ni while Te was eluted with dilute HCl [13].

56.2 DETERMINATION TECHNIQUES

Atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* $0.5 \mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 oxidizing (lean, blue) flame at the most sensitive 214.3 nm line. The signal is suppressed by large excess of Ca, Cu, Si, Na, Zn and Zr and matrix matching is required. An EDL is available but offers hardly any gain in sensitivity. Quartz furnace AAS offers a DL of 0.02 ng ml^{-1} on atomization of TeH_2 [5]. Dimethyl- and diethyltellurium were determined by GC QF AAS, with ADLs in the low nanogram range [14]. Graphite furnace AAS offers an ADL of 1 pg. Tellurium losses in the drying–ashing step are common unless a suitable matrix modifier, e.g. Pd [8,11], Pd– $\text{Mg}(\text{NO}_3)_2$ [15], H_2PtCl_6 [16] or Ni [9], is used. Inter-

ferences can be eliminated by trapping TeH_2 in the GF [3] or extraction [8]. A silver-coated graphite atomizer has been recommended for the determination of Te in organic matrices [17].

Plasma source atomic emission spectrometry

Plasma source AES offers a DL of 50 ng ml^{-1} at the most intensive 214.28 and 238.58 nm ICP emission lines. The former is interfered with by Cu. Hydride generation is preferred for sample introduction, often in multielement mode (*cf.* Part II). The HG DCP AES determination of Te has been optimized [6].

Mass spectrometry

Natural Te consists of eight isotopes (the most important are ^{130}Te , ^{128}Te , and ^{126}Te) whereas ^{127}Te (0.87%) is unstable with a half-life of *ca* 10^{13} years. The sensitivity of ICP MS is poor; ^{130}Te is the most sensitive. Tellurium isotopes ^{130}Te and ^{126}Te have been determined by ETV ICP MS with a DL of $5\text{--}10 \text{ ng ml}^{-1}$ [18]. Trace amounts of Te were determined by the redox sub-superequivalence method of ID analysis with a DL of $2 \mu\text{g ml}^{-1}$ [19]. *On-line* addition of enriched Te (^{125}Te) as an internal standard for automated ID ICP MS determination of Te in waste waters has been developed [20]. Spark source ID MS has been used for the analysis of copper [21]. Isotope dilution GC MS after enrichment with ^{120}Te and derivatization with (4-fluorophenyl)magnesium bromide has been proposed [7].

Fluorescence techniques

A FI ND AFS using an Ar-H_2 flame was reported to give an ADL of 0.02 ng for TeH_2 [22]. Electrothermal LE AFS was reported to achieve an ADL of 20 fg; molecular backgrounds from nitric oxide and silicon monoxide have been discussed [23].

56.3 ANALYSIS OF REAL SAMPLES

Analytical procedures for the determination of Te are summarized in Table 56.1.

Environmental materials

Elemental Te^0 and gaseous forms of Te(IV) and Te(VI) can be adsorbed on gold-coated beads [12] and charcoal [27] but at higher flow

TABLE 56.1

Combined procedures for the determination of tellurium

Sample (amount)	Sample decomposition	Separation	Detection	DL	Ref.
Air	none	sorption on Au-coated beads, selective leaching, cation exchange to separate Te(VI) and Te(IV)	GF AAS	0.03 ng/m ³	12
Aerosols (0.1 g)	HNO ₃ -HClO ₄	matrix removal by cation exchange	GF AAS	n.g.	13, 24
Sea, rain water (4 l)	none	copptn. with Mg(OH) ₂ , volatn. as TeH ₂	GF AAS	60 pg/l	3
Seawater (0.05 l)	none	volatn. as TeH ₂ and trapping in a GF	GF AAS	2-4 pg	1
Geochemical (1 g)	HNO ₃ -HClO ₄	extrn. with xanthate (cyclohexane), back-extrn. (HNO ₃)	GF AAS	8 ng/g	9
Urine (1 ml)	HNO ₃ -H ₂ O ₂	extrn. with bis(tri-fluoroethyl)-DTC (toluene), derivatization with (4-fluoro-phenyl)MgBr	GC ID MS	n.g.	7
Urine (50 ml)	HNO ₃ -HClO ₄	extrn. of TeCl ₄ (MIBK)	GF AAS	0.1 ng/ml	8
Urine	HClO ₄ -HNO ₃	volatn. as TeH ₂	QF AAS	1 ng	2, 25
Blood	HNO ₃	extrn. into MIBK	GF AAS	1 ng/ml	26
Tissues	hyamine hydroxide	none	GF AAS	170 ng/g	16
Bio and aerosol (0.2 g)	HNO ₃ -HClO ₄ - HCl-HF	volatn. as TeH ₂ , trapping in GF	GF AAS	2-4 pg	1
Iron		copptn. with Pd	GF AAS	10 ng	11
Pb-based alloys (2 g)	HNO ₃ -HClO ₄	pptn. of Pb as PbCl ₂ ; copptn. as Te ⁰ with As	GF AAS	n.g.	5
Pb-based alloys (10 g)	HNO ₃ -HClO ₄	pptn. of Pb as PbCl ₂ ; volatn. as TeH ₂	QF AAS	n.g.	5

rates the efficiency of the gold-coated beads decreases, in contrast to charcoal [27]. The species can be thermally desorbed or selectively leached with water [Te(VI)], 1 M HCl [Te(IV)] and 3 M HNO₃ (Te⁰) [27]. Graphite furnace AAS is the usual determination technique [12,27]. In natural waters Te needs to be preconcentrated, e.g. by coprecipitation with Mg(OH)₂ [3] or volatilization followed by trapping of TeH₂ in a GF [1]. Adsorption and colloidal behaviour of Te(VI) in aquatic solutions has been discussed [28]. Preliminary results of Te speciation in wastewater by LC ICP MS have been presented [29].

Biological materials

Clinical samples require digestion (usually by HNO₃) to enable extraction of TeCl₄ [8] or volatilization of TeH₂ [2]. Detection limits in direct analysis are a factor of 10 poorer [16]. Tellurium has been determined by GF AAS in blood plasma of rabbits with a DL of 1 ng ml⁻¹ [30]. Graphite furnace AAS and HG AAS have been compared for the determination of Te in urine [31]. The use of stable and radioactive isotopes for the determination of biokinetic parameters of Te in rabbits has been compared; tracer solutions enriched in stable (¹²⁴Te or ¹²⁶Te) and radioactive (^{121m}Te or ^{123m}Te) isotopes were administered to animals followed by the analysis of the blood samples by SIMS and γ -ray spectrometry [26].

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Thallium

Thallium (Tl, atomic weight 204.37, melting point 303°C, $d = 11.85 \text{ g cm}^{-3}$) is silvery grey, soft metal. It occurs in the earth's crust with an average abundance of 0.3–0.5 ppm, primarily in sulphide ores and potassium minerals. The metal dissolves readily in H_2SO_4 and in dilute HNO_3 to form the corresponding Tl(I) salts. Thallium exists in the I and III oxidation states; the former being more stable. Thallium(III) hydrolyzes readily; the Tl^{3+} ion is only present in strong acids. Thallium(III) is readily reduced to Tl(I) by H_2S , SO_2 and NH_2OH . Zinc, Al and Mg metals precipitate Tl^0 as black powder. Strong oxidants such as Br_2 oxidize Tl(I) to Tl(III), especially in the presence of excess of Br^- or Cl^- which stabilize the Tl(III) formed. Thallium(III) forms halide, oxalate and tartrate complexes. The need for trace determination of Tl exists, apart from geochemical studies, in eco- and clinical toxicology [1]. The analytical chemistry of Tl has been reviewed [2,3].

57.1 SEPARATION AND PRECONCENTRATION

Extraction

Thallium(III) is usually extracted from halide media with oxygen-containing solvents as TlCl_4^- [4–6], TlBr_4^- [7,8] or TlI_4^- [9]. The selectivity can be improved in ternary systems (containing e.g. *n*-octylamine [5,9] or TPPO [6]). Reductants interfere [10]. The Tl can be stripped from the organic phase with a reductant, e.g. Na_2SO_3 solution. [8]. Thallium can be extracted with DDTC into toluene or MIBK [11].

Sorption

Sorption of Tl(III) as TlCl_4^- from oxidizing (containing Br_2 or Ce(IV)) media onto a strongly basic anion exchanger is popular [12–14]. Thallium is eluted with reducing solutions [12,13]. Sorption of the ion pair of TlCl_4^- with a quaternary ammonium ion on C_{18} -bonded silica has been reported [15].

Coprecipitation

Coprecipitation of Tl(III) with Mn(II) (on oxidation with MnO_4^-) has been proposed [10]. Thallium can be electrodeposited as Tl^0 on the cathode and as Tl_2O_3 on the anode [16,17]. An ASV flow cell has been designed [18]. Thallium(I) was precipitated as TlI or Tl_2CrO_4 [19].

57.2 DETERMINATION TECHNIQUES

Spectrophotometry

Thallium(III) halide complexes react in acid medium (1–2 M HCl) with basic dyes, e.g. Rhodamine B or Brilliant Green, to form ion associates extractable into organic solvents [20]. The method is sensitive ($\epsilon \approx 10^5$) and the selectivity can be considerably improved by extraction of TlBr_4^- with DIPE followed by shaking the organic phase with a dye solution.

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of $0.7 \mu\text{g ml}^{-1}$ in the recommended air– C_2H_2 oxidizing (lean, blue) flame at the most sensitive 276.8 nm line. An EDL is available but no gain in sensitivity is obtained. Flame AAS is often combined with an extraction step [7,8].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers a DL of 0.1 ng ml^{-1} (characteristic mass 7 pg) using pyrocoated tubes and platform atomization, but it is affected by losses, especially in the presence of chloride. The latter promotes the formation of volatile TlCl in the pyrolysis and the atomization stages [21]. The chloride interference can be removed in the presence of a high concentration of H_2SO_4 [9,10,22–25] which allows ashing at 600°C . A higher pyrolysis temperature ($850\text{--}950^\circ\text{C}$) is achieved with Pd based modifiers [26–31], often in combination with ascorbic acid [30,31] or $\text{Mg}(\text{NO}_3)_2$ [11,26,28,29]. The Pd modification alone is often not suffi-

cient for chloride-rich matrices (seawater, urine) [21,27,32]. Abandoning the pyrolysis step [27] or pyrolyzing the modifier prior to pipetting the sample and purging with H_2 have been recommended [21]. Signal depression in oxidizing acid media was reported to be alleviated with a reducing agent (ascorbic acid, NH_2OH or glycerol) [11] or by the use of carbide-coated tubes [33]. Modification of the furnace by chemisorption of oxygen was recommended to prevent the formation of volatile Tl_2O and thus volatilization losses [34]. An Mo microtube atomizer has been studied [35].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 30–50 ng ml⁻¹ at the most sensitive 276.79 nm and 190.86 nm lines and is seldom used unless in a multielement array (*cf.* Part II). The 190.86 nm line should not be used for Al-rich matrices. The Tl(I) 276.79 nm line was found to have the lowest background in a Cd matrix [36]. Overlaps of V and Cr at 276.79 nm can be treated by the interfering element correction method.

Atomic fluorescence spectrometry

Electrothermal LE AFS offers a DL in the low fg range (3–15 fg) which is controlled by contamination [24,37–39]. Atomization from a L'vov platform has been recommended [24,37]. The interferences due to HCl and $HClO_4$ have been eliminated using tungsten carbide coated tubes and a W matrix modifier [39]. The interference of Ca has been corrected by the method of standard additions [37].

Mass spectrometry

Thallium has two stable isotopes, ^{203}Tl and ^{205}Tl , with relative abundances of 29.53% and 70.47%, respectively. Thermal ionization MS is well suited owing to the high yield of the Tl ionization [16,17,40]. Inductively coupled plasma MS offers sensitivities in the low ng/g in FI [41] or ETV [4] mode. Isotope dilution considerably improves accuracy [41]. In the presence of Pb concentrations higher than 500 $\mu g g^{-1}$, the separation of Tl by extraction of $TlCl_4^-$ into MIBK is recommended [4].

Neutron activation analysis

Irradiation of ^{205}Tl gives rise to a short-lived ^{206}Tl ($t_{1/2} = 4.2$ min) and long-lived ^{204}Tl ($t_{1/2} = 3.6$ y) nuclides which are pure β -emitters. Radiochemical separation is required and detection limits are poor.

57.3 ANALYSIS OF REAL SAMPLES

Environmental and geological samples

Ambient air contains less than 1 ng m^{-3} Tl [42]. The concentration in sea and natural waters is estimated at 0.01 ng l^{-1} [43]. These levels are too low to be determined directly so preconcentration, usually by anion exchange, is required [12,13]. Avoidance of HClO_4 during the decomposition is recommended as it suppresses the GF AAS signal [29,30]. Sulphuric acid has been used as volatilization suppressant during the LiBO_2 fusion decomposition of fly ash [23] and sediment lecheates [10]. A speciation study of Tl in river sediments showed that Tl is largely found in the HNO_3 -leachable and the oxalate-leachable fractions [10]. For non-contaminated geochemical samples preconcentration of Tl is required to match the sensitivity of instrumental techniques. Relevant analytical procedures are summarized in Table 57.1.

Biological samples

Direct Zeeman GF AAS offers a sensitivity of $0.2\text{--}1 \text{ ng ml}^{-1}$ for urine [11,30,45] and *ca* $5\text{--}10 \text{ ng ml}^{-1}$ for blood and serum [25] under STPF conditions. Extraction with DDTC into MIBK is indispensable to reach a DL of 0.02 ng ml^{-1} [11]. These values do not match the normal subject levels but are sufficient for patients with acute intoxication [11]. Results of comparison studies of Tl in urine have been published [45]. Significant losses were observed after 60 d storage. The content of Tl in food is regulated at the 0.1 ppm (fresh weight) level [1]. Electrothermal AAS and ETA LE AFS have been compared for the determination of Tl in dissolved and slurried food and agricultural samples [37]. The use of a rapidly heated tube atomizer equipped with a L'vov platform, H_2SO_4 as a modifier and the charring of the sample to reduce scattered radiation has been recommended for biomaterials [37]. H_2SO_4 was used as a matrix modifier to reduce chloride interferences in the determination of Tl in biological samples [9,25,37]. Analytical procedures developed for the determination of Tl in biological samples are summarized in Table 57.2.

Industrial samples

Thallium is determined in Al, Cd, Ni and Zn alloys usually directly after sample decomposition [36,41,46] or on extraction of Tl(III) halide [6,8] by FAAS [8], GF AAS [46], ICP AES [6,36] and ICP MS [41]. Multielement procedures including Tl are reported in the tables in Part II.

TABLE 57.1

Determination of thallium in environmental and geological samples

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Coastal, estuarine water (10 l)	none	anion exchange as TlCl_4^-	GF AAS	n.g.	12
Tap, mineral, rain, ground water (10 l)	none	anion exchange as TlCl_4^-	GF AAS	0.003	13
Rocks, soils, sediments (2 g)	HF , <i>aqua regia</i> , $\text{HBr}-\text{Br}_2$	extraciton as TlBr_4^- (MIBK)	FAAS	200	7
Sediments (0.5 g)	$\text{HF}-\text{HNO}_3$	anion exchange as TlCl_4^-	GF AAS	n.g.	12
River sediments	selective leaching (speciation)	coprecipitation with MnO_2aq	GF AAS	n.g.	10
River sediments	HNO_3-HF , <i>aqua regia</i> (bomb)	electrolysis	ID TI MS	n.g.	17
Soils (0.5 g)	$\text{HF}-\text{HNO}_3$	anion exchange as TlCl_4^-	FAAS	40	14
Ores (0.5–1 g)	HNO_3-HF (bomb)	anion exchange as TlCl_4^- , extraction with Rhodamine B	VIS	n.g.	44
CRM river, lake sediments, soil (0.1–1 g)	HNO_3-HF (bomb)	electrolysis	ID TI MS	0.1 ^a	16
CRM rocks and sediments (0.25–1 g)	$\text{HF}-\text{HCl}-\text{HClO}_4$, fusion with LiBO_2 or $\text{HF}-\text{HCl}-\text{HNO}_3$	extraction as TlCl_4^- (MIBK)	ID ETV ICP MS	6	4
CRM fly ash (0.6 g)	fusion with LiBO_2 in the presence of H_2SO_4	none	GF AAS	n.g.	23

^a Absolute detection limit, ng.

TABLE 57.2

Determination of thallium in biological samples

Sample	Digestion	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Urine (1–5 ml)	none	extraction with DDTC (MIBK)	GF AAS	0.02	11
Urine (25 ml)	none	extraction as TlI_4^- with <i>n</i> -octylamine (<i>n</i> -BuAc)	GF AAS	0.3	9
Urine (25 ml)	HNO_3 - H_2O_2	extraction as $TlCl_4^-$ (DIBK)	GF AAS	0.2	32
Hay, green algae, lucerne (10 g)	dry ashing, dissoln. in HCl	sorption on C_{18} column as ion pair of $TlCl_4^-$ with <i>N</i> -(1-carbaethoxypenta- decyl)trimethylammo- nium, elution with EtOH	FAES	0.1	15
CRM animal tissues (0.3 g)	HNO_3 (bomb)	precipitation as TlI , extraction as $HTlBr_4$, precipitation as Tl_2CrO_4	RNAA	1	19
CRM plant, animal tissues (0.1–1 g)	LTA, dissoln. in HNO_3 - HF	electrolysis	ID TI MS	100 ^a	16
Rat tissue, feces (0.2–1.0 g)	HNO_3	none	GF AAS	5 ^b	25

^a Absolute detection limit, pg; ^b in the analyzed solution, ng/ml.

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Thorium

Thorium (atomic weight 232.04, melting point 1750°C, $d = 11.7 \text{ g cm}^{-3}$) is a silvery-grey metal. Thorium is a natural radioactive element, fairly abundant in the earth's crust (13 ppm), occurring primarily in monazite ores. The low energy of the radiation means that special precautions are not required. Of the six isotopes present in nature (^{227}Th , ^{228}Th , ^{230}Th , ^{231}Th , ^{232}Th and ^{234}Th) the most stable is ^{232}Th ($t_{1/2} = 1.4 \times 10^{10} \text{ y}$). The metal is passivated by HNO_3 . It readily dissolves in $\text{HNO}_3\text{--HCl}$, $\text{HNO}_3\text{--HF}$ mixtures, in concentrated H_2SO_4 and in molten $\text{K}_2\text{S}_2\text{O}_7$. In analytical properties Th resembles Zr, Ti and the REE. The only oxidation state of Th is IV. In non-complexing media at $\text{pH} < 1$ Th exists as the Th^{4+} ion. In less acidic solutions it is hydrolyzed (less readily than Ti and Zr) with formation of simple and polymeric hydroxo species. Thorium hydroxide, $\text{Th}(\text{OH})_4$, which precipitates at $\text{pH } 3.5\text{--}4$ is insoluble in excess of alkali but dissolves in dilute acids. In acidic solutions Th forms strong complexes with oxalate, tartrate, citrate, EDTA, sulphate and nitrate.

58.1 SEPARATION AND PRECONCENTRATION

Separation and preconcentration procedures older than 1985 have been reviewed [1].

Solvent extraction

Thorium is one of the few multivalent metals [besides Au(III) , Ce(IV) , U(VI) and Cr(VI)] which are extractable as nitrate complexes from HNO_3 solutions by oxygen-containing solvents, e.g. MIBK or ethyl acetate [1]. Other common extractants include TBP [2,3], mesityl oxide

[4], TTA [3,5], TPAO [6] in non-polar solvents. Fluoride interferes and must be masked, e.g. as AlF_6^{3-} . The TTA extraction is inhibited by Fe(III) which needs to be reduced to Fe(II), e.g. with ascorbic acid [5]. Supercritical fluid extraction of Th with fluorinated β -diketones and TBP has been developed [7].

Coprecipitation

Traces of Th can be precipitated as $\text{Th}(\text{OH})_4$ with $\text{NH}_3(\text{aq})$ ($\text{pH} > 4$) using Fe(III) as collector [1,8–10]. The precipitation of the Th oxalate or ThF_4 from a weakly acid medium with La, Ce or Ca as collectors is an alternative (REE and U(IV) coprecipitate). Thorium can be separated from the REE and other metals by precipitation of the iodate from 1 M HNO_3 in the presence of tartaric acid and H_2O_2 using a Ce(IV) collector [11]. Electrodeposition of Th from alkaline solutions and TBP is the end step of α -spectrometric procedures [12].

Sorption and chromatographic methods

Various sorbents for Th have been reviewed [13]; charcoal [13] and cellulose–Hyphan [14] were recommended. Separation of the Th nitrate complex on strong basic anion exchangers is popular [10,15–17], especially for radiochemical purification. Strong acidic cation exchangers can be used alternatively; Th is fairly selectively retained from 3–4 M HCl and can be then eluted with, e.g. HNO_3 [18]. Reverse-phase cation pair HPLC of a polyhalogenated bisazo chromotropic acid derivative for the separation of REE, Th and Cr has been developed [19]. Thorium forms volatile complexes with 1,3-diketones which can be separated by GC [13].

58.2 DETERMINATION TECHNIQUES

Methods for the trace determination of Th have been compiled [6]. Radiochemical NAA and ICP MS are most sensitive; the latter is becoming definitely the method of choice for most materials. No reliable AAS method has so far been developed because of serious carbide formation problems, especially in a graphite tube.

Spectrophotometry

Arsenazo III reacts with Th in strongly acidic solution to form a grey–green water soluble complex. The maximum absorbance is obtained at 8 M HCl, but the reaction in 3 M HCl ($\epsilon = 1.15 \times 10^5$ at 655 nm)

in the presence of oxalate is more selective (Zr, Hf and Nb do not interfere). Uranium (IV) is oxidized to U(VI) which does not interfere [3]. Trace elements must be separated prior to analysis [3,14]. Sub- $\mu\text{g/g}$ (ng/ml) DLs for water can be obtained [3,6,20].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of $1\text{--}5\text{ ng ml}^{-1}$ at the most sensitive (283.279 and 283.73 nm) emission lines [21]. Interferences have been comprehensively discussed; several metals interfere [1]. At the trace level Th must be separated, e.g. by extraction with ethylacetate or coprecipitation with $\text{Fe}(\text{OH})_3$ [1].

Mass spectrometry

Thermal ionization MS offers an ADL of $0.1\text{--}0.2\text{ ng}$ [6,17] but requires a careful purification of the analyte. The ^{230}Th spike is used for the determination of ^{232}Th . The ^{229}Th spike can be used alternatively so that both ^{230}Th and ^{232}Th signals can be measured in the same run and the mass fractionation can be corrected for [17]. Inductively coupled plasma MS offers a DL of *ca* 1 pg ml^{-1} [22,23] which can be decreased down to 1 fg ml^{-1} using high resolution equipment and ultrasonic nebulization [8]. The most abundant ^{232}Th nuclide is usually measured. If low levels of ^{230}Th need to be measured the ^{232}Th should be skipped to avoid detector overload and the 231 mass needs to be monitored to ensure no tailing from ^{232}Th [15]. Isotope dilution analysis is possible using ^{230}Th as a spike but resolution problems may occur [24]. ^{205}Tl and ^{209}Bi are commonly added as internal standards [2,22]. Formation of Th hydride under ICP MS conditions has been studied [25].

α -Spectrometry

The nuclides ^{230}Th , ^{232}Th and ^{234}Th which are weak α -emitters are clumsily measured *via* natural decay. The isotopic ratio can be determined [16] but large samples and cumbersome separation–preconcentration are generally required. The Th fraction must be free of α -emitters (e.g. Si, Fe, Al) [16]. The standard method involves a long chromatographic separation of Th followed by electroplating onto a silver planchette and takes 3–4 days and counting times up to 2 weeks [15]. Detection limits down to 1 ppb in solids can be achieved but a large uncertainty in terms of blank and background exists. Direct determination of ^{228}Th by high resolution γ -spectrometry of its daughter ^{212}Pb has been developed [16].

Neutron activation analysis

Irradiation of Th produces ^{233}Pa ($t_{1/2} = 27\text{d}$, $E_{\gamma} = 312\text{ keV}$) according to the reaction $^{232}\text{Th}(n,\gamma)^{233}\text{Th} \rightarrow \beta^{-} \rightarrow ^{233}\text{Pa}$ [26]. The ^{233}Pa emits both β and γ radiation; the latter is usually measured. Possible spectral interferences with the ^{233}Pa counting have been exhaustively discussed [9]. Instrumental NAA of simple matrices offers a DL of 1 ng g^{-1} after short irradiation and 40 h of counting [27]. Pre- and postirradiation separation is common in RNAA [9]. Yields have been monitored with ^{230}Th and ^{231}Pa tracers [9].

Miscellaneous

Fluorinated β -diketone complexes can be determined by GC ECD [3]. Microgram levels of Th can be determined on separation–preconcentration by WD XRF [13] or ED XRF [28,29].

58.3 ANALYSIS OF REAL SAMPLES

The relatively stable nuclides (^{228}Th , ^{230}Th , ^{232}Th , ^{234}Th) can be determined directly whereas the concentrations of the short lived ones, ^{227}Th and ^{231}Th , are dictated by the concentrations of their progenitors. Trace level analysis requires a class 100 environment and cleaning Al foil. Blanks need to be run on a regular basis [9].

Environmental and biological materials

Thorium in air can be determined by ED XRF of the filters with a DL of 20–50 μg for industrial hygiene purposes [28]. Environmental concerns [37] and geochemistry of Th in the marine environment have been discussed [10,16]. Results of an interlaboratory comparison study of the determination of total Th and its isotopes in rocks have been presented [30]. Determination of Th in terrestrial waters by ICP MS and HR ICP MS has been compared [8]. Thorium can be readily determined in a variety of biomaterials by direct feeding of the acid digestate into the ICP MS with a DL down to 1 pg ml^{-1} [22–24,31]. A summary of Th levels measured in human tissues has been published [32]. Analytical methods are summarized in Table 58.1.

Industrial samples

Thorium is an α -emitter and can spoil characteristics of electronic devices. Instrumental NAA, GD MS and ICP MS have been compared

TABLE 58.1

Methods for the determination of thorium in environmental and biological materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (pg/g)	Ref.
Sea water (10 l)	none	coprecipitation with $\text{Fe}(\text{OH})_3$, double anion exchange, extraction of Pa from HCl (DIBK), extraction with TTA	RNAA	7 ^a	9
Spring (5 l)	none	evaporation, coprecipitation with $\text{Fe}(\text{OH})_3$, anion exchange, electroplating	α -spec	n.g.	35
Effluents		copptn. with Ce iodate	VIS	n.g.	11
Sediment (1 g); pore water	HF-HCl-HNO ₃	anion exchange, coprecipitation with $\text{Fe}(\text{OH})_3$, anion exchange, electro-deposition	α -spec	0.07	10
Mine water (4 ml), soil (0.1 g)	none	SFE with TTA-TBP	RNAA	n.g.	7
Coal ash (0.5 g)	HF-HNO ₃ , HClO ₄ -HNO ₃	extraction with TTA (benzene), back extraction (HNO ₃)	ICP AES	11 ^b	5
Soil (0.5 g)	HF-HNO ₃ -HClO ₄	sorption	ICP MS	n.g.	33
Marine sediments (1 g)	HCl, HClO ₄ , HF, HNO ₃	anion exchange	ICP MS	9	15
Sediments (30-40 g)	HNO ₃ -NaNO ₂	anion exchange	γ - and α -spec	n.g.	34
CRM diet	HNO ₃	anion exchange; coprecipitation of Pa with BaSO ₄	RNAA	0.05 ^c	30

^a In the solution, fg/l; ^b in the solution, ng/ml; ^c absolute detection limit, ng.

TABLE 58.2

Methods for trace determination of Th in industrial materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Glass (500 mg)	HF	volatilization of the matrix as SiF ₄ , BF ₃	ICP MS	1	3
Glass (500 mg)	HClO ₄ -HF-H ₃ BO ₃	voltatilization of the matrix as SiF ₄ , BF ₃ , separation of Zr by extraction with TTA, extraction of Th with TTA-TBP	VIS	20	3, 20
Glass (5 g)	HClO ₄ -HF-H ₃ BO ₃	extraction with FOD-TBP (toluene), GC	ECD	3000	3
Polyimide, SiC, alum-inium oxide (0.1-0.2 g)	HF-HNO ₃ (bomb); HCl (bomb) (Al ₂ O ₃)	anion exchange	RNAA	0.01-0.1	40
Aluminium (1-5 g)	HNO ₃ -HCl	extraction with mesityl oxide; back extraction (H ₂ O)	ICP MS	few	4
Aluminium (0.1 g)	HCl	removal of ²⁴ Na on Sb ₂ O ₅ , cation exchange	RNAA	0.05	37
Aluminium (10 g)	HCl (Cu catalyst)-H ₂ O ₂	extraction with TBP (cyclohexane), back extraction H ₂ O	ICP MS	0.008	2
Aluminium (10 g)	HNO ₃	extraction with ethyl acetate (solvent ashing)	ICP AES	8	1
Aluminium (5 g)	NaOH	coprecipitation with Fe(OH) ₃	ICP AES	5	1
Aluminium (3 g)	HNO ₃	anion exchange of ²³³ Pa; extraction of Pa with TOPO	RNAA	0.01	38
Tungsten (0.1 g)	HF-HNO ₃	anion exchange of ²³³ Pa	RNAA	1.2	39
Tantalum	HF	cation exchange	RNAA	n.g.	18

FOD = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.

for the analysis of high purity aluminium [4]. Instrumental NAA gives a DL of 6 ng g^{-1} which decreases to 0.4 ng g^{-1} upon removal of ^{24}Na (on Sb_2O_5) [36] and, further to 0.05 ng g^{-1} by a two-step cation exchange [37]. ICP MS in CF nebulization mode is not sufficient for the sub-ng/g levels but LA ICP MS proved to be successful [19]. ICP AES, spectrophotometry and chelate-GC for the analysis of glass have been compared [3]. Combined procedures are summarized in Table 58.2.

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Tin

Tin (atomic weight 118.7, melting point 238°C, $d = 7.28 \text{ g cm}^{-3}$) is a shiny white metal (β -allotropic form). It occurs in the earth's crust with an average abundance of 2–3 ppm, primarily in cassiterite (SnO_2). The metal dissolves rapidly in hot HCl, hot concentrated H_2SO_4 , dilute HNO_3 and in dilute alkali metal hydroxides (with evolution of H_2). Concentrated HNO_3 oxidizes Sn to the β -form of hydrated SnO_2 , called metastannic acid. Tin exists in oxidation states –IV (in SnH_4), II and IV. Tin(II) may exist as the Sn^{2+} ion in acidic solutions which tends to hydrolyze at lower acidities. Alkalis precipitate from solutions of Sn(II) and Sn(IV) hydrated SnO and SnO_2 , respectively, which are soluble in excess of alkali. Tin(II) is a reductant both in acidic and in alkaline media. Tin(II) and Sn(IV) tend to form chloride complexes. Tin(IV) forms a series of organotin compounds of the type $\text{R}_n\text{Sn}^{(4-n)+}$, where $n = 1, 2, 3$ or 4 and R denotes an alkyl (Me, Et, Pr, Bu, Oc), phenyl or cyclohexyl group. Trace analysis for tin is important in geochemistry and because of environmental concerns. As the toxicity of Sn is strongly species dependent, speciation of tin in environmental and biological matrices is essential.

59.1 SEPARATION AND PRECONCENTRATION

Volatilization

Tin(IV) hydride (SnH_4 , stannane) is generated in acid media in the presence of NaBH_4 . Various mineral (HClO_4 , HNO_3 , HCl, H_3PO_4) and organic (tartaric, succinic, oxalic, malic, acetic) acids have been investigated [1]. Dilute HNO_3 seems to be the best choice [1–3]. The reaction is hampered by transition metals (Fe, Co, Ni, Cu, Ag, Au). Iron is

masked effectively by succinic acid [1] or phen [4], whereas malic acid masks Cu and Ni [1]. Masking with L-cystine was found to be inefficient in removing the interferences from Au, Pd and Pt [2]. Organotin compounds interfere with HG determination of Sn(II) and must be pre-separated [5]. Stannane can be generated in organic media, e.g. in CHCl_3 extracts mixed with a DMF solution of NaBH_4 and H_2SO_4 [6]. The stannane can be preconcentrated by trapping cryogenically [7] or in a graphite furnace [8].

Other methods

Tin(IV) can be extracted from HCl medium into MIBK [9,10]. Other extractants included tropolone (toluene) [11], N-nitrophenylhydroxylamine (CHCl_3) [6], BPHA (toluene) [12] and TOA (heptane–amyl acetate) [13]. Coprecipitation of tin as hydrous stannic oxide with $\text{MnO}_2(\text{aq})$ or $\text{Y}(\text{OH})_3$ is widely used [14]. Both Sn(II) and Sn(IV) are retained as the chloride complexes [3] and Sn(IV) is retained as the oxalatocomplex [15] from HCl medium on anion exchangers.

59.2 DETERMINATION TECHNIQUES

Spectrophotometry

Tin(IV) reacts with phenylfluorone at a pH of 1–1.2 to form an orange–red sol ($\epsilon = 7.7 \times 10^4$ at 550 nm). More sensitive are methods based on the ion associates of tin halide complexes with basic dyes. All the methods shows poor selectivity and must be preceded by separation of tin.

Flame and quartz furnace atomic absorption spectrometry

A $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame [11,12,16–18] is preferred to an air C_2H_2 –flame [6,19]. The 224.6 nm [6,18,20–23], 286.3 nm [10,12], 235.5 nm [9,17] lines are all used. An EDL is available but it offers hardly any gain in sensitivity. A sensitivity of $3 \mu\text{g ml}^{-1}$ is observed. Quartz furnace AAS offers an ADL of 0.1 ng (4 ng ml^{-1}) with the introduction of SnH_4 [3,4,24]. This is a favourable detection technique for GC of organotin [25–33].

Graphite furnace atomic absorption spectrometry

An ADL down to a few pg (DL ca 0.2 ng ml^{-1}) can be obtained but the determination is plagued by volatilization losses, interaction with the graphite tube and vapour phase interferences (especially from sulphate). Volatilization losses are minimized by matrix modification with

noble metals, especially Pd, in the presence of hydroxylamine [34–40]. Other modifiers included Pd–Mg [41], $(\text{NH}_4)_2\text{HPO}_4$ – $\text{Mg}(\text{NO}_3)_2$ – HNO_3 [10,42,43], $\text{K}_2\text{Cr}_2\text{O}_7$ – $\text{NH}_4\text{H}_2\text{PO}_4$ – HNO_3 [44] and picric acid [11]. Pre-treatment of the graphite furnace with carbide-forming elements (e.g. W, Nb, Ta and Y) was proposed to increase the atomization efficiency [14,21,45]. The use of pyrolytic graphite tubes with platforms is essential to achieve high sensitivity [13,35]. Metal sulphates almost completely suppress the Sn signal, whereas $(\text{NH}_4)_2\text{SO}_4$ enhances it [42,44]. Ascorbic acid is a common modifier to minimize interferences from the chloride, nitrate or sulphate [23,46] but the use of concentrated solutions of ascorbic acid resulted in a build-up of carbonaceous residue [44]. In general, the sensitivity is matrix dependent so the standard additions method is advised to achieve good accuracy [13,35].

Atomic emission spectrometry

The most sensitive emission 188.99-nm line ($\text{DL } ca\ 15\ \text{ng ml}^{-1}$) is overlapped by Fe. Other lines, 235.48 nm, 242.95 nm and 284.00 nm, are half as sensitive and interfered with by Fe (284.00 and 242.95 nm), Cr (284.00 nm) and Co (235.45 and 242.95 nm). The hydride generation mode offers an increase in sensitivity by a factor of *ca* 3 orders of magnitude in ICP AES [1,47] or DCP [2] and the virtual freedom from spectral interferences.

Mass spectrometry

Tin has 10 stable isotopes: ^{112}Sn (0.97%), ^{114}Sn (0.65%), ^{115}Sn (0.36%), ^{116}Sn (14.5%), ^{117}Sn (7.7%), ^{118}Sn (24.2%), ^{119}Sn (8.6%), ^{120}Sn (32.6%), ^{122}Sn (4.6%) and ^{124}Sn (5.8%). All but ^{118}Sn and ^{120}Sn are subject to isobaric overlaps with Cd, In and Te nuclides. Either ^{118}Sn and ^{120}Sn or both need to be therefore monitored [34,35,48]. In ID ICP MS the altered $^{118}\text{Sn}/^{120}\text{Sn}$ isotope ratio was measured [35].

Fluorescence

Hydride generation coupled with F AFS significantly reduces the light scattering that occurs with the nebulization of solutions and allows a DL of $1\ \text{ng ml}^{-1}$ to be obtained [49]. Most organotin compounds show a similar response to that of inorganic tin [50].

Neutron activation analysis

Neutron activation analysis is based on the counting of two radionuclides: ^{117m}Sn ($t_{1/2} = 14\ \text{d}$, $E_\gamma = 158.44\ \text{keV}$) and ^{113}Sn ($t_{1/2} = 112\ \text{d}$) [51].

The sensitivities are fairly poor because of the low cross-section; a radiochemical separation of Sn is required.

59.3 ANALYSIS OF REAL SAMPLES

Water samples

Water samples have been evaporated with HNO_3 and H_2SO_4 to prevent the hydrolysis of tin [4]. A pretreatment with $\text{HNO}_3\text{--Br}_2$ was recommended to decompose organotin compounds [50]. Direct atomization of sea [37], fresh [34] or drinking [34,41] water with suitable matrix modifiers with a DL at the sub-ng/ml level has been reported. In general, Sn should be separated from the seawater matrix prior to GF AAS [20]. A DL of 0.05–01 ng ml⁻¹ has been reported for direct ICP MS of terrestrial and drinking water [34]. Toluene-extractable organotin was determined in effluents by ZGF AAS using Pd matrix modifier with a DL 40 of ng/l [40]. Combined procedures for total tin are scarce and are based on hydride generation [50].

Geological samples

Geological samples contain inorganic tin as a constituent of the silicate lattice or as a highly resistant Sn(IV) oxide (cassiterite). Ignition with NH_4I converts the cassiterite into SnI_4 without attacking the lattice-bound tin [10]; conversely, the silicate lattice may be attacked by an acid mixture without attacking the cassiterite [8,24,34]; the total tin can be determined after fusion with LiBO_2 [9,10,52] or $\text{Li}_2\text{CO}_3\text{--H}_3\text{BO}_3$ [15]. The acid attack can be facilitated by prior removal of silicon as SiF_4 (by heating with HF in the presence of H_2SO_4 to prevent tin losses) [13]. Tin is determined in the digest directly [34,52] or on enrichment [12,13, 15]. A comparison study of several procedures has been presented; in the presence of cassiterite or Sn(II) sulphide only XRF and ICP AES provided accurate results, down to a DL of 2 µg g⁻¹ [53]. Combined procedures for the determination of tin in geochemical samples are summarized in Table 59.1.

Biological materials

Tin is present in human tissue in quantities reaching a few hundred µg/g [54]. These levels are accessible by GF AAS upon LTA [24] or wet ashing with $\text{HNO}_3\text{--HClO}_4$ [23], directly [23] or on extraction with MIBK [22]. The DL of ICP MS in serum (0.05 ng ml⁻¹) is controlled by

TABLE 59.1

Determination of tin in geological samples

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Atmospheric particulates	$\text{HNO}_3\text{--H}_2\text{SO}_4$, HF	volatilization as SnH_4	QF AAS	0.2 ^a	24
Soils, rocks, sediments (1 g)	fusion with LiBO_2 , dissolution in HCl	extraction with TOPO (MIBK)	FAAS	1	9
Rocks (0.5 g)	fusion with NaCN	extraction with BPHA (toluene)	FAAS	n.g.	12
CRM rocks (CRMs) (0.2 g)	fusion with $\text{Li}_2\text{CO}_3\text{--H}_3\text{BO}_3$	anion exchange as oxalate complex	GF AAS	n.g.	15
CRM rocks (0.1 g)	fusion with LiBO_2 , dissolution in HCl	extraction with TOPO (MIBK)	GF AAS	0.2	10
Marine sediments (0.5 g)	$\text{HNO}_3\text{--HF--}$ HClO_4 (bomb)	volatilization as SnH_4 , trapping in a GF	GF AAS	0.4	8
Rocks (CRMs) (0.1–0.2 g)	Si removal as SiF_4 , fusion with LiBO_2	extraction with TOA (heptane– AmAc)	GF AAS	n.g.	13

^a ng/m^3

the blank [48]. Leaching of Sn from the organic matter with boiling HCl has been recommended [16]. The HCl– HNO_3 attack allows for more complete digestion and significantly reduces the burner-clogging problem in canned foods [17]. Losses of tin from boiling $\text{HNO}_3\text{--HCl}$ due to the precipitation of Sn as metastannic acid and volatilization of SnCl_4 have been reported [19]. Losses of SnCl_2 can be minimized by predigestion (charring) with H_2SO_4 and then digestion with $\text{H}_2\text{SO}_4\text{--HNO}_3$ and H_2O_2 [19]. Direct analysis of the digest, usually by GF AAS, is favoured over hydride generation which is severely affected by the acid concentration in the digest [19,23]. Total tin has been determined in plant or animal tissue by GF AAS or ICP MS after wet acid digestion with a DL of $0.05 \mu\text{g g}^{-1}$ [34,35,43,45]. Different separation and detection modali-

TABLE 59.2

Combined procedures for the determination of total tin in biological tissues

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
Blood, plasma, tissue	LTA or HNO_3 - HClO_4	extrn. into MIBK	GF AAS	0.2 ^a	22
Human tissue	HNO_3 - HClO_4 - CCl_3COOH	volatn. as SnH_4	ICP AES	0.03 ^b	47
CRM marine tissue (0.5 g)	HNO_3 , HF- HClO_4	volatn. as SnH_4 , trapping in a GF	GF AAS	0.02	8
CRM fish tissue (10 g)	leaching with HCl - NaCl (EtAc)	volatn. as SnH_4	QF AAS	0.01 ^b	5
CRM plant, wheat, rice flour (2 g)	HNO_3 - HClO_4 - H_2SO_4 - NH_4VO_3	volatn. as SnH_4	ICP AES	0.05 ^b	1
Fruit juices, plant	leaching with HCl	extrn. with <i>N</i> -nitrosophenyl-hydroxylamine (CHCl_3), volatn. as SnH_4	FAAS	n.g.	6
Canned foods (5 g)	H_2SO_4 , H_2SO_4 - HNO_3 , H_2O_2	volatn. as SnH_4	FAAS	0.2	19
Canned foods (5 g)	HNO_3 - HCl	anion exchange, volatn. as SnH_4	FI QF AAS	0.08 ^b	3

^a Absolute detection limit, ng; ^b in the analyzed solution, $\mu\text{g/ml}$.

ties for the NAA analysis of biomaterials have been discussed [51]. Combined procedures for the determination of total tin in biomaterials are summarized in Table 59.2.

Industrial materials

Polymers can be analyzed by FAAS on mineralization [18]. During the dissolution of alloys in HNO_3 tin forms the hardly soluble metastannic acid; citric acid was added to keep Sn in solution [55]. Hydride generation used for the analysis of steel is strongly affected by the pH

TABLE 59.3

Determination of tin in industrial materials

Material (amount)	Dissolution	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
CRM alloys (0.5 g)	$\text{HNO}_3\text{--HCl}$	volatilization as SnH_4	ICP AES	0.05 ^b	1
CRM copper, iron, steel (0.1–2 g)	HNO_3	volatilization as SnH_4	DCP AES	0.02 ^b	2
Al-based alloys	HCl	extraction with N-nitrosophenyl-hydroxylamine (CHCl_3), volatilization as SnH_4	FAAS	n.g.	6
Steels (0.1–0.5 g)	$\text{HNO}_3\text{--HCl}$	volatilization as SnH_4	ND AFS	1.2 ^a	49
Zinc metal (0.5 g)	$\text{HNO}_3\text{--HCl}$	coprecipitation with $\text{Y}(\text{OH})_3$	GF AAS	n.g.	14
High purity gallium (0.1–0.25 g)	$\text{HNO}_3\text{--HCl}$ (bomb)	volatilization as SnH_4 , trapping in AgNO_3	GF AAS	n.g.	57
High purity selenium	HNO_3	matrix removal by reduction with N_2H_4	GF AAS	0.05	55

^a Absolute detection limit, ng; ^b in the analyzed solution, $\mu\text{g/ml}$.

dependence of the interference from Ni and Co [56]. Combined procedures for the determination of Sn in industrial materials are summarized in Table 59.3.

Accuracy concerns

Contamination from plastic bottles, pipette tips etc. is common even after careful washing and rinsing. Teflon containers used for digestions should be checked for Sn content after each set of determinations. Severe memory effects were encountered in the hydride generation in an automatic system so manual apparatus was used [24]. Tin hydrides

are susceptible to adsorption, polypropylene is able to absorb SnCl_2 [24]. A high blank of the H_2O_2 precluded its use in sample digestion [24]. Samples should not be stored in acid concentrations lower than 0.7 M for extended periods owing to the possibility of hydrolysis of Sn(IV) of which products polymerize and are difficult to dissolve [3,4]. Care must be taken to prevent volatilization of tin; evaporation of sample solutions to dryness should be avoided.

59.4 SPECIATION

A viable analytical method should allow the determination of the target compounds without any interference from other organotin species at levels of $<0.1 \text{ ng l}^{-1}$ for water and $<1 \text{ ng g}^{-1}$ for dry solid materials. The valid approaches combine a separation technique such as GC, HPLC or SFC coupled with an AAS, AES, FPD or MS detection [7,58,59]. Sample preparation methodologies fall in two basic categories: these based on *in-situ* derivatization by NaBH_4 followed by purging and cryotrapping of the derivatized analytes [7] and those based on the extraction of the ionic organotin compounds, either native or after complexing them or *in-situ* derivatizing [59].

59.4.1 Sample preparation

Extraction

Extraction with HCl , HBr and acetic acid succeeds for trisubstituted organotins (e.g. TBT, TPhT, tricyclohexyltin (TCyT)) but fails for more polar species. Solvent extraction with tropolone or DDTC using a non polar solvent is the usual choice. Tropolone is preferred to DDTC as under acidic conditions ($\text{pH} < 4$) the latter undergoes decomposition, giving rise to extractable interferents [60]. Solid-phase extraction (SPE) procedures [61–68] allow a higher preconcentration factor and ease of application in field and *on-line* systems but only filtered samples can be analyzed. Extraction can be combined with derivatization *in situ* [29, 69–72]. Sodium tetraethylborate (NaBEt_4) [71,72] is preferred to NaBH_4 [70] as a derivatization reagent because of larger freedom of interferences. Supercritical fluid extraction of hexylated butyl- and phenyltin species was reported [69].

Derivatization

The methods for the conversion of ionic alkyltins into gas chromatographable species include: (1) *in-situ* hydridization using NaBH_4 or ethylation with NaBEt_4 [7,29,71–73], (2) derivatization using Grignard reagents: methyl- [74–76], ethyl- [25,26,61–63,77,78], propyl- [79], pentyl- [27,28,60,64,80–82] or hexyl- [69,83] magnesium chlorides or bromides, and (3) halogenation [84–86]. Some methods imply the formation of the volatile species in the extract [29,70] or on the solid phase support [65,87]. Ethylation and pentylation are the usual choices as they allow a simultaneous speciation analysis of methyl-, propyl-, butyl- and phenyl-tin species.

Cleanup

Extracts of samples rich in organic matter contain coextractives (fats, high boiling hydrocarbons) which may deposit on the column influencing the separation, or increasing the detector background. The advent of more selective detectors has reduced the need for cleanup procedures but nevertheless in some cases they cannot be avoided. The cleanup procedures are mostly based on ion-exchange or reversed phase chromatography (e.g. using Alumina, Silica gel or Sep-Pak C_{18} columns). An effective method of reducing the need for the loss prone cleanup is to decompose organic matrix by enzymatic hydrolysis or to separate it from the analytes by back extraction [88].

59.4.2 Instrumental techniques

Gas chromatography based techniques

Purge-and-trap thermal desorption based on *in-situ* conversion of ionic organotin to hydrides cryogenically trapped on a sorbent and then released on heating has been reviewed [8,89]. QF–AAS is primarily used for the detection of stannanes [7,90] as for higher boiling species the interface and detection conditions are much more critical [28,60, 91,92]. An ADL down to a few pg can be obtained. Tin gives strong emission in a hydrogen-rich flame in the 360–490 nm (blue) and in the 600–640 nm (red) regions. Measurements in the latter region are preferred. With appropriate interference filters (e.g. 610 nm), used good selectivity against hydrocarbons and good sensitivity (ADL down to a few pg) are obtained. The sensitivity of FPD can be increased by measuring the quartz surface induced luminescence (QSIL) at 390 nm [93]. The specificity of GC–FPD can be enhanced by splitting half of the

GC effluent to a DCP emission spectrometer [94]. Of plasmas investigated for the atomization of organotin compounds in the GC effluent the widest popularity was gained by the MIP. ADLs of 0.05–6 pg have been reported [27,78,95]. Gas chromatography–EI MS is widely applied; an ADL down to 1 pg is common [74].

Liquid chromatography based techniques

The use of HPLC for the separation of organotin compounds has been reviewed [58] and apparently the HPLC based techniques suffer from poor resolution and usually a lack of sensitivity. Liquid chromatography techniques based on cation exchange [86,96–100], reversed phase [101,102] and ion interaction [103–105] separation have been developed but applications to real samples are remarkably scanty, problems being found with real sample matrices. ICP MS is practically the only detection technique able to cope with the levels in real samples.

59.4.3 Speciation analysis of real samples

Organotin can be extracted directly from water samples whereas customized approaches are required for sediments and biotissues. As organotin compounds are not involved in mineralogical processes and bind onto the surface of the sediment, the complete dissolution of the latter prior to the analysis is not considered necessary. The basic approach to release organotin compounds from the sediment involves acid leaching (HCl, HBr, HAc) in an aqueous or methanolic medium by sonification, stirring, shaking or Soxhlet extraction with an organic solvent. To increase the extraction yield the addition of a complexing agent (tropolone, DDTC) is mandatory. Various analytical techniques for the recovery of organotin compounds from biological matrices have been compared. The stability of organotin in the samples, the DDTC extraction and the chromatographic purification step as well as possible evaporation losses have been examined [106]. Enzymatic or TMAH hydrolysis is favoured over acid leaching. Procedures for water, sediments and biotissues are summarized in Tables 59.4, 59.5 and 59.6, respectively.

Sources of error

Possible errors arising during sampling and storage have been reviewed [107]. The most important problems in speciation analysis for organotin compounds are apparently the adsorption onto and the release

TABLE 59.4

Selected methods for organotin speciation analysis in water

Species	Extraction reagents (solvent)	Derivatization agent	Detection	DL (pg/ml as Sn)	Ref.
TBT, DBT, MBT, TPhT, DPhT, MPhT	acetic acid/acetate, pH 5, NaBEt ₄ (hexane)	NaBEt ₄	GC MIP AES	0.1	72
TBT, DBT, MBT	Tris/acetic acid, pH 6, NaBEt ₄ (iso-octane)	NaBEt ₄	GC FPD	0.4	71
TBT, DBT, MBT, TPhT, DPhT, MPhT	tropolone (dichloromethane)	PeMgBr	GC FPD	2	81
TBT, DBT, MBT, TPhT, DPhT, MPhT	HCl, tropolone (hexane)	MeMgCl	GC FPD	0.5–6	74
TBT, DBT, MBT, TPhT, DPhT, MPhT, TCyT, DCyT, MCyT	HCl, ascorbic acid, Sep-PAK C ₁₈ cartridge, tropolone (diethyl ether)	EtMgCl	GC FPD GC FPD GC FPD	0.01 3.5–8 17–50	61– 63
TBT, DBT, MBT, TPhT, DPhT, MPhT	HBr, tropolone (pentane)	PeMgBr	GC FPD	20–50	80
TBT, DBT, MBT, TMT, DMT, MMT	HCl, NaCl, tropolone (hexane)	EtMgCl	QF AAS	5	25
TBT, DBT, MBT	HCl, pH 1, NaCl, tropolone (toluene)	EtMgCl	QF AAS	40	26
TBT, DBT, TPhT, DPhT, MBT, MPhT	HCl–THF (1+3), NaCl, tropolone (benzene)	PrMgCl	GC FPD	3	79
TBT, DBT, MBT, TMT, DMT, MMT	citric acid/phosphate, pH 5, NaDDTC (pentane)	PeMgBr	GC QF AAS GC MIP AES	0.4–0.8 0.01	27, 28
TBT, DBT, MBT	Carbopack or LC18, H ₂ O, tropolone (methanol)	PeMgBr	GC FPD GC QF AAS	2 10	64
TBT, DBT, MBT, TPhT, DPhT, MPhT	C ₁₈ , citrate–ammonia pH 9, NaBEt ₄ (methanol)	on-column NaBEt ₄	GC MIP AES	0.1– 0.2	65

continued

TABLE 59.4 (continuation)

Species	Extraction reagents (solvent)	Derivatization agent	Detection	DL (pg/ml as Sn)	Ref.
DBT, TBT, TPT	sorption on ODS column, elution with MeOH	morin	HPLC ^a FLU	n.g.	99
Sn(II), Sn(IV), TBT	none	none	HPLC ^a FAAS	n.g.	100
MMT, MBT, DMT, DBT, DPT, TMT, TBT, TPT			HPLC ^b FAAS	n.g.	101

^a Cation exchange chromatography; ^b reversed-phase chromatography.

TPhT, DPhT, MPhT = tri-, di- and monophenyltin.

TBT, DBT, MBT = tri-, di- and monobutyltin.

TCyT, DCyT, MCyT = tri-, di- and monocyclohexyltin.

TMT, DMT, MMT = tri-, di- and monomethyltin.

of some organotin species from certain sample container materials (e.g. PVC) and the poor recoveries of the analytes. The use of polycarbonate and glass [108] was favoured over that of polyethylene. An increase in particulate load can make the recoveries lower and irreproducible which, in particular, is observed during sediment analysis. Individual organotin compounds may bind to components present in a sediment to a degree varying with the salinity and the amount of particulate matter present in the water column [109], which may make a method that is valid for one sediment ineffective for another [77]. The recovery of butyltin compounds from the PACS-1 reference sediment in ten different procedures has been examined [77].

Interlaboratory comparison studies

Interlaboratory comparison studies have resulted in the issue of CRMs for TBT, DBT and MBT in sediment is a marine harbour sediment (PACS-1) prepared by the National Research Council of Canada with concentrations of 1.21 ± 0.24 for TBT, 1.14 ± 0.20 for DBT and 0.28 ± 0.17 for MBT ($\mu\text{g g}^{-1}$ as Sn, in dry sample). The National Institute for Environmental Studies (NIES, Japan) issued a CRM 11, which is a fish tissue with a certified content of $1.3 \pm 0.1 \mu\text{g g}^{-1}$ for TBT and a reference value of $6.3 \mu\text{g g}^{-1}$ for TPhT (both values given as chlorides).

TABLE 59.5

Methods for organotin speciation analysis in sediments

Species	Extraction reagents (solvent)	Derivatization agent	Detection	DL (ng/g as Sn)	Ref.
TBT, DBT	HCl/MeOH (cyclohexane)	NaBH ₄	GC FPD	50	70
TBT, DBT, MBT	acetic acid/acetate, pH 5, NaBEt ₄ (hexane)	NaBEt ₄	GC QF AAS	n.g.	73
TBT, DBT, MBT, TPhT, DPhT, MPhT, TCyT, DCyT, MCyT	HCl, tropolone (dichloromethane)	NaBEt ₄	GC QF AAS	n.g.	29
TBT, DBT, MBT, TPhT, DPhT, MPhT	in situ hexylation, SFE	HeMgBr	GC FPD	n.g.	69
TBT, DBT, MBT	MeOH-HCl, tropolone, sonication (toluene/isobutyl acetate)	—	GC FPD	30	84
TBT, DBT, MBT, TPhT, DPhT, MPhT, TCyT,	HCl, tropolone (diethyl ether)	EtMgCl	GC FPD	0.01–0.02–0.7	61–63
TBT, DBT, MBT, TPhT, DPhT, MPhT		MeMgCl	GC FPD, GC MS	0.1–2	74
TBT, DBT, MBT	HCl, HBr, tropolone (pentane)	PeMgBr	GC FPD	3	82
TBT, DBT, MBT, TMT, DMT, MMT	H ₂ O, NaCl, KI, sodium benzoate, tropolone (hexane)	EtMgCl	GC QF AAS	5	25
TBT, DBT, MBT	HCl, NaCl, tropolone (toluene), 4 h	EtMgCl	GC QF AAS	2	26
TBT, DBT, TPhT, DPhT, MBT, MPhT	HCl-THF (1+11), tropolone (benzene)	PrMgCl	GC FPD	0.5	79
TBT, DBT, MBT	H ₂ O, acetic acid, NaDDTC (hexane)	PeMgBr	GC QF AAS GC MIP AED	0.45 0.01–0.08	27, 28
TBT, TPT, TET			HPLC LEI		97
DBT, TBT	MeOH-HCl (hexane–isobutyl acetate)	none	HPLC ICP MS		86
MBT, DBT, TBT			HPLC GF AAS		98

For abbreviations, see Table 59.4.

TABLE 59.6

Methods for the speciation analysis in biological tissues

Analytes	Sample	Preparation	Extraction (solvent)/ derivatization	Detection	DL (ng/g as Sn)	Ref.
Butyl, methyl	mussels, oyster, fish	enzymic hydrolysis (lipase, protease)	dithizone (C ₂ H ₂ Cl ₂ / hexane), MeMgCl or BuMgCl	GC QF AAS	0.2–0.8	30
Butyl	oyster	leaching with HCl	tropolone (C ₂ H ₂ Cl ₂), NaBH ₄	GC QF AAS	0.5–3.5	31
Butyl	mussel, oyster	leaching with HCl–MeOH	NaBH ₄ (purge- and-trap)	GC QF AAS	2–3	90
Butyl	fish	HCl–MeOH	hexane, MeMgCl	GC FPD	20	75
Butyl, Phenyl, Cyclohexyl, Octyl	wine, beer	enzymic hydrolysis (pepsin)	tropolone (pentane), MeMgCl	GC QF AAS	0.05	32, 33
Butyl	fish, clams	homogenization (hexane) with HCl/acetone		GC FPD/DCP	n.g.	94
Phenyl	potatoes	equilibration with hexane	(hexane), MeMgCl	GC FPD	n.g.	76
TET, DET, MET	mammalian tissue			HPLC ^a FAAS	n.g.	96

TET, DET, MET = tri-, di- and monoethyltin.

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Titanium

Titanium (Ti, atomic weight 47.90, melting point 1670°C, $d = 4.5 \text{ g cm}^{-3}$) is a silver-grey metal. It occurs in the earth's crust with an abundance of 0.6%, primarily in ilmenite (iron titanate) and rutile (TiO_2). The metal is protected by an oxide film which makes it insoluble in cold mineral acids and alkalis. It dissolves in HF, hot HCl, H_2SO_4 , concentrated H_3PO_4 , oxalic and formic acids. The most stable oxidation states are III and IV. The former is a strong reductant and is readily oxidized to the stable Ti(IV). No simple Ti^{4+} ion exists. The hydrolyzed Ti(IV) species is usually referred to as the titanyl ion, TiO^{2+} . At $\text{pH} \geq 1$ basic salts precipitate, followed by the amorphous $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$, often referred to as hydroxide $[\text{Ti}(\text{OH})_4]$ or orthotitanic acid (H_4TiO_4). Titanium (IV) forms fluoride, citrate, oxalate, EDTA and peroxide complexes. In view of subpercentage concentration in geochemical solid samples and Ti alloys, and the absolute biological indifference of Ti the only trace analysis studies have focused on natural waters [1].

60.1 ANALYTICAL TECHNIQUES

The need to preconcentrate Ti exists only in ultratrace analysis of natural waters. Chelating resins were used [2–4].

Spectrophotometry

None of the common methods is suitable for trace analysis of real samples because of either poor sensitivity or interference (at least from Fe(III)). The method based on the reaction of Ti with chromotropic acid in weak acidic media ($\epsilon = 1.7 \times 10^4$ at 460 nm) is widely used provided that Fe(III) is either separated or reduced.

Atomic absorption spectrometry

Flame AAS has a sensitivity of *ca* 2 $\mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O-C}_2\text{H}_2$ (reducing, rich, red) flame at the most sensitive 364.3, 365.4 and 320.0 nm lines. Ionization should be controlled by the addition of an alkali metal salt (e.g. KCl). The Ti signal is increased in the presence of many metals. Graphite furnace AAS requires pyrolytic graphite coated tubes [5] but practical use is difficult owing to carbide formation and memory effect [5,6].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of *ca* 1 ng ml^{-1} at the most sensitive 334.94, 336.12 and 323.45 nm lines which are overlapped by Cr, Co and Ni, respectively. In addition, the Ti measurement at 334.94 nm is hampered by the spectral interference from a weak Ti line at 334.90 nm if a poorly resolving monochromator is used. In the latter case the 336.12 nm line is the usual choice [7].

Inductively coupled plasma mass spectrometry

Titanium has five naturally occurring stable isotopes: ^{46}Ti (8.01%), ^{47}Ti (7.33%), ^{48}Ti (73.81%), ^{49}Ti (5.5%) and ^{50}Ti (5.34%). Isobaric interferences have been comprehensively discussed [4]. The most abundant ^{48}Ti nuclide is overlapped by ^{48}Ca (0.19% natural abundance). ^{49}Ti -enriched Ti was used as the spike [4]. The instrumental detection limit is 0.2 ng ml^{-1} which can be decreased to 0.02 ng ml^{-1} using high resolution equipment [4]. ICP MS is a convenient GC detector for titanium porphyrins [8].

Neutron activation analysis

Neutron activation analysis lacks a suitable isotope. The only available isotope, ^{51}Ti ($t_{1/2} = 5.79$ min, $E_\gamma = 0.32$ MeV), is short lived.

60.2 ANALYSIS OF REAL SAMPLES

Because of the extremely low solubility of Ti compounds, its concentrations in fresh and coastal waters are low, generally below 1 ng ml^{-1} [9]. Open ocean concentrations of Ti are up to four orders of magnitude lower than this [3]. Titanium in fresh water and seawater is determined electrochemically, using cathodic adsorption stripping voltammetry, with a DL of 0.01 ng ml^{-1} [10] sufficient for fresh water analysis [9,10]. In

open ocean water it is determined after preconcentration on chelating resins followed by ICP MS (DL 5 pg l⁻¹) [3,4]. Stringent precautions involving purification of acids by double distillation in a sub-boiling quartz still, vapour phase transition of NH₃(aq), and purification of other reagents on chelating resins are mandatory. Selective detection of Ti porphyrins in coal and oil shale has been reported [8].

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Transuranium elements

Transuranium elements (TEs) include elements with atomic numbers higher than 92. The most important are neptunium (Np), plutonium (Pu), americium (Am) and curium (Cm) which are environmental contaminants. The nuclides of interest include $^{238-241}\text{Pu}$, ^{237}Np , ^{241}Am and ^{242}Cm . All TEs are artificial and enter the environment as fall-out from weapon testing, nuclear waste disposal and various nuclear accidents. Plutonium can exist in III, IV, V and VI oxidation states. Pu(III) is easily oxidized to Pu(IV) with NaNO_2 and H_2O_2 while Pu(V,VI) are reduced to Pu(IV) with NaNO_2 ; the reactions are slow and uncomplete. Plutonium forms stable fluoride complexes which can interfere in the subsequent separation/preconcentration steps. Low concentrations and complicated chemical behaviour under complex ecological conditions make the analytical chemistry of TEs challenging. Transuranium elements have been the subject of a recent comprehensive work [1]. Environmental levels of transuranic nuclides have been summarized [2]. Progress in analytical chemistry of actinides has been reviewed [3,4].

61.1 SEPARATION AND PRECONCENTRATION

Separation techniques for actinides were reviewed, with particular emphasis on Pu [5].

Coprecipitation

Coprecipitation of TE as hydroxides with Fe(II) [6] (under reducing conditions), Fe(III) [7–9] or Ce [10] as carriers, as oxalates with CaC_2O_4 [8,11], fluorides (with LaF_3 [12,13], CeF_3 [9] or NdF_3 [14]) and phosphates (with BiPO_4 [12,15,16]) is the most common preconcentration

method. The REE fluorides precipitate Pu(III and IV) but leave in solution Pu(V,VI) [17]. Di-, tri- and tetravalent actinides are coprecipitated on BaSO₄ while penta- and hexavalent forms remain in solution [18]. Electrodeposition of ²³⁹Pu on a metal disk from alkaline solutions and TBP [19] is the end step of procedures involving α -spectrometry.

Extraction

Extraction of the TE with TTA is the most popular separation technique [4,12,13,20–23]. Other extractants include long-chain trialkyl amines [24,25], TOPO [10] and di(2-ethylhexyl)sulphoxide [25] in non-polar solvents (benzene, xylene). Plutonium can be stripped upon reduction to Pu(III) with NH₄I–HCl solution. Methods for extraction of Am have been referenced [26]. Progress in the extraction chemistry of the actinides has been discussed [27].

Chromatographic techniques

Extraction chromatography using TBP [28–31] or TOPO [32] as stationary phases from concentrated HNO₃ or HCl is widely used. The common alternative is the retention of the Pu(NO₃)₆^{2–} complex from 8 M HNO₃ on an anion exchange column while most other elements including other actinides are eluted [3,9,33]. Plutonium(IV) and Pu(V) exhibit very different sorption behaviour so the transport is dependent on oxidation state [31]. Reduction of Pu(V) to Pu(IV) with NaNO₂ is commonly applied. Plutonium is eluted on reduction to Pu(III) using a NH₄I–HCl [8,33] or HI–HCl [32] mixtures. Carrier mediated transport of TEs through liquid and plasticized membranes has been reviewed [34].

61.2 DETERMINATION TECHNIQUES

α -Spectrometry has long been the only analytical technique for environmentally relevant levels of TEs but in recent years ICP–MS has been rapidly gaining in popularity [20–22,35–39]. These techniques have been compared for the determination of the Pu isotopes [20], ²³⁷Np [21,22] and Am [35]. Atomic absorption spectrometry is impossible because of the radioactive sources required. ICP AES detection limits for ²³⁷Np, ²³⁹Pu, ²⁴¹Am and ²⁴⁸Cm have been discussed [17,40]. Plutonium and Np can be determined with a DL of 30–50 ng ml^{–1} whereas Am and Cm can be detected at levels down to 1–5 ng ml^{–1} [40]. Large amounts of U interfere [17]. For Np INAA based on the ²³⁷Np(n, γ)²³⁸Np reaction is feasible [21].

α -Spectrometry

Simultaneous and sequential determination of Np, Pu, Am and Cm has discussed [53]. α -Spectrometry of ^{237}Np demands a high degree of purity to avoid interference from ^{234}U , ^{231}Pa and ^{230}Th [41]. The ^{238}Pu and $^{239,240}\text{Pu}$ are easily resolved but ^{239}Pu and ^{240}Pu α -energies are too close to be separated by conventional α -spectrometry [8]. ^{239}Np , ^{242}Pu and ^{243}Am , have been used as yield tracers [8,9,23]. Natural U does not interfere with the measurements of $^{238-240}\text{Pu}$ [8]. $^{241}\text{Americium}$ ($t_{1/2} = 433\text{ y}$) is in principle an α -emitter but also a weak γ -emitter [42]. Liquid scintillation counting α -spectrometry has been developed for ^{241}Pu [41].

Inductively coupled plasma mass spectrometry

The ^{239}Pu and ^{240}Pu are easily distinguished but ^{238}Pu suffers from isobaric interference from the naturally occurring enormous excess of ^{238}U [20]. Meticulous removal of U is thus necessary. Further, the formation of uranium hydride in the nebulizer (at a level of some 10^{-5} of the ^{238}U peak) implies that at least a partial removal of ^{238}U is necessary if an acceptably low DL is to be achieved for ^{239}Pu . $^{242}\text{Plutonium}$ is used both as a chemical yield tracer and as a spike in the MS. In the case of ^{237}Np there are no potential isobars but ^{238}U may overlap [21–23]. $^{239}\text{Neptunium}$ (short-lived γ -emitter) is used as the chemical yield tracer and ^{236}U is added to determine the MS efficiency. An ADL of 15 fg is achieved for ETV ICP MS if the 236–244 mass range is scanned. It can be decreased to 1 fg in single ion monitoring mode [19]. A DL of 7 fg for ^{243}Am has been reported [36]. Detection limits for ^{239}Pu are 0.08, 0.09 and 0.01 mBq ml $^{-1}$ for ICP MS, HR ICP MS and HR ICP MS with ultrasonic nebulization, respectively [43]. For ^{237}Np the respective values of 0.01, 0.001 and 0.00005 mBq ml $^{-1}$ were reported (1 mBq = 0.01 ng) [43].

61.3 ANALYSIS OF ENVIRONMENTAL SAMPLES

Waters

The behaviour of the actinides in the environment has been discussed [44], with emphasis on speciation of TE [9,45]. Speciation of Pu in natural waters is governed by redox reactions, hydrolysis, complexation and polymerization [46,47]. Actinides in the V oxidation state: Pu(V), Np(V) are dominant in true solutions whereas Am(III), Pu(IV and VI) hydrolyze and sorb onto colloids and suspended particles [9]. The organic humic matter can reduce Pu(VI) rapidly while Pu(V) is

TABLE 61.1

Analytical procedures for the determination of transuranium elements in water

Water (amount)	Separation and/or preconcentration	Detection	Nuclide (DL)	Ref.
Fresh, sea (50 l)	coprecipitation with $\text{Fe}(\text{OH})_3$, dissolution in HNO_3 -HF, anion exchange, coprecipitation with CeF_3	α -spec	$^{238-240}\text{Pu}$ (5 $\mu\text{Bq/l}$)	8
Fresh, sea (50 l)	coprecipitation with CaC_2O_4 , $\text{Fe}(\text{OH})_3$, anion exchange, extraction with TTA; coprecipitation with CeF_3	α -spec	Am, Cm	8
Sea (200 l)	coprecipitation with $\text{Fe}(\text{OH})_2$, dissoln. in HCl - HNO_3 , anion exchange	α -spec	$^{239, 240}\text{Pu}$	6
Lake (25 l)	coprecipitation with $\text{Fe}(\text{OH})_3$, anion exchange, cation exchange, electrodeposition	α -spec	$^{239, 240}\text{Pu}$, ^{241}Am , ^{242}Cm	9
Fresh (400 l)	coprecipitation with $\text{Fe}(\text{OH})_3$, anion exchange, coprecipitation of Am and Cm with oxalate, anion exchange, electrodeposition	α -spec	$^{239, 240}\text{Pu}$, ^{241}Am , ^{242}Cm	48

reduced slowly [47]. Analytical procedures usually involve preconcentration of TE from large amounts of water (up to 200 l) by sorption on an anion-exchanger followed by the purification of the nuclides for α -spectrometry (Table 61.1).

Other materials

Separation of TEs from soil, sediment and biotissues is realized by direct leaching by mineral acids from samples calcinated at 550°C . This is insufficient for insoluble compounds (Pu oxides) which require a complete attack. Plutonium attracts the largest attention and has been the subject of the reviews with an emphasis on ecological materials [5,49] and human tissues [50]. α -Spectrometry is the most widely used for Pu and Am in biota [7,8,51,52] and for ^{241}Am in foodstuffs and human tissue [53]. Analytical procedures are summarized in Table 61.2.

TABLE 61.2

Analytical methods for the determination of transuranium elements in ecological materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	Nuclide (DL)	Ref.
Airborne effluents	ashing of filter, dissoln. in $\text{HNO}_3\text{--HF--HCl}$	anion exchange, copptn. with LaF_3 , extrn. with TTA, electroplating	α -spec	$^{238}, ^{239}, ^{240}\text{Pu}$	12
Airborne effluents	ashing of filter, dissoln. in $\text{HNO}_3\text{--HF--HCl}$	copptn. with BiPO_4 , extrn. with HDEHP (toluene), TTA (benzene), electroplating	α -Spec	^{241}Am , ^{242}Cm , ^{244}Cm	12
Soil	ashing, dissoln. in HF--HNO_3	anion exchange, copptn. with LaF_3 , extrn. with TTA, electroplating	α -spec	Pu	13
Soil (10 g)	leaching with $\text{HNO}_3\text{--HF--Al(NO}_3)_2$	extrn. chrom. on TOPO on silica gel and copptn. with LaF_3	α -spec	$^{239}, ^{240}\text{Pu}$	14
Soil	leaching with HNO_3	extrn. of ^{237}Np in TTA, copptn. with Fe(OH)_3 , extrn. with TBP, anion exchange	ICP MS	^{237}Np (5 n Bq/ml), ^{239}Pu (10 $\mu\text{Bq/ml}$), ^{240}Pu (32 $\mu\text{Bq/ml}$)	23
Soil, ashed biota	ashing, leaching with HNO_3	copptn. with CaC_2O_4 or with LaF_3	γ -spec	Am (1Bq/kg soil; 0.1 Bq/kg biota)	42
Soil, sediment, mussel (1–20g)	HCl--HNO_3	extrn. of Fe (DIPE); anion exchange; extrn with TTA	ETV ICP MS	$^{239}, ^{240}\text{Pu}$ (15 fg) ^{237}Np	20

continued

TABLE 61.2 (*continuation*)

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	Nuclide (DL)	Ref.
Soil, sediment (50 g)	ashing, leaching with HNO ₃ , dissoln. in HNO ₃ -H ₂ O ₂ , HF	anion exchange, copptn. with CeF ₃	α-spec	5 μBq/g	8
Soil, sediment (1-200 g)	ashing, leaching with HCl-HNO ₃	anion exchange	ICP MS	²³⁷ Np (1 pg/ml)	38
Sediment (100 g)	ashing, leaching with HCl-HNO ₃	anion exchange, extrn. of Np(IV) with TTA, back extrn.	ICP MS, RNAA	²³⁷ Np (0.1- 0.6 pg/g)	21
Sediment (5-10 g)	ashing	anion exchange, extrn. by cyclo- hexanone.	MS techniques	²³⁷ Np, ²³⁹ , ²⁴⁰ Pu, ²⁴¹ Am	43
Biomaterials, foodstuffs (0.5 kg)	ashing, HNO ₃ , H ₂ O ₂ , HF	anion exchange, copptn. with CeF ₃	α-spec	0.5 μBq/g	8
Grass	enzymic hydrolysis, H ₂ O ₂ alkaline digestion	heating with 10% KOH, enzymolysis at pH 5.6-5.8, fermentation with Daher's yeast, digestion with 30% H ₂ O ₂	α-spec	²³⁸ Pu, ²³⁹ , ²⁴⁰ Pu, ²⁴¹ Am	51
Ores (0.1 g)	fusion KF, K ₂ S ₂ O ₇ , dissoln. in DTPA	copptn. as hydroxide with Ce, extrn. with TOPO, anion exchange, electrodeposition	α-spec	(n.g.)	10
Bones	HNO ₃ -H ₂ O ₂	pptn. with CaC ₂ O ₄ , extrn. with 10 M HCl, electroplating	α-spec	Pu	11

^a μBq/g; ^b μBq/ml; ^c ADL, fg.

Quality control and assurance

The large sample volumes required make the detection limits usually blank controlled. An interlaboratory comparison of ^{239}Pu and ^{240}Pu in human tissue was reported [54]. There is a serious lack of natural matrix CRMs for the actinides and ^{237}Np in particular. Certified reference materials for Pu have been discussed [55]. The SRM 4350B River sediment and SRM 4353 Soil with homogeneous $^{239,240}\text{Pu}$ and ^{241}Am distribution can be used. Human tissues: SRM 4351 (lung) and SRM 4352 (liver) are available but there is significant inhomogeneity for $^{239,240}\text{Pu}$ since this element is taken in particulate form.

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Tungsten

Tungsten (W, atomic weight 183.86, melting point 3400°C, $d = 19.3 \text{ g cm}^{-3}$) is a silvery grey metal. It occurs in the earth's crust at an average concentration of 60 ppm, mainly in wolframite and scheelite. The metal reacts slowly with concentrated H_2SO_4 , HNO_3 and *aqua regia*. It dissolves rapidly in a HNO_3 –HF mixture, in H_2O_2 (with formation of peroxotungstic acid) and in fused alkalis in the presence of an oxidizing agent. The only common oxidation state of W is VI. In strongly alkaline media W exists as the tungstate (WO_4^{2-}). On acidification the hydrated oxide precipitates which is soluble in concentrated HCl and in alkaline solutions. Tungsten forms heteropolyacids with many elements (e.g. P, Si, V) and peroxide, citrate, tartrate, oxalate, phosphate and fluoride complexes. Tungsten(VI) can be reduced with Zn or Sn(II) in concentrated HCl to tungsten blue, a mixture of W(V) and W(VI).

62.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Traces of W can be separated by precipitation with $\text{NH}_3(\text{aq})$ (excess to be avoided) with Fe(III) or Al as collectors but extraction or sorption are simpler and offer a better selectivity. Extraction of W has been discussed [1]. Extraction with α -benzoinoxime [2] and BPHA [3,4] into CHCl_3 from acid media is the most popular (Mo, Nb and Ta are co-extracted). Extraction of the ion associate between tungstate and Fe(II)-2,2'-dipyridyl has been reported [5]. Sorption of W on chelating [6,7] or chelate-loaded [8] resins or sorption of W chelates on charcoal [9–11] are used alternatively.

Spectrophotometry

Tungsten is commonly determined on reduction to W(V) (usually by

SnCl_2) and extraction of its complex with SCN^- into *iso*-pentanol ($\epsilon = 1.56 \times 10^4$ at 403 nm) or by extraction of its complex with dithiol into pentylacetate ($\epsilon = 1.92 \times 10^4$ at 640 nm) [12,13]. Both the thiocyanate and the dithiol methods are non-selective and are also used for Mo (*cf.* Chapter 37); proper choice of conditions allows either metal to be determined in the presence of the other. First-derivative solid-phase spectrophotometry based on the complex of W with pyrocatechol violet has been proposed [14].

Atomic absorption spectrometry

The sensitivity of FAAS in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame is poor (10 and 20 $\mu\text{g ml}^{-1}$ at the 255.1 and 400.9 nm lines, respectively). It is generally insufficient for trace analysis unless after extraction of W into MIBK [15]. Sulphate enhances the W signal probably by preventing the formation of metallic clotlets and thus allowing easier atomization [16]. Calcium was found to depress the W signal owing to the formation of the refractory calcium tungstate but sodium silicate was an effective releasing agent [16]. Tungsten was determined by FAAS indirectly on extraction of the WO_4^{2-} -Fe(II)-dipyridyl ion associate and the determination of the stripped iron [5]. Graphite furnace AAS is not feasible for W because of the formation of refractory carbides.

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 20–30 ng ml^{-1} at the most sensitive 207.91, 209.48, 218.94 and 224.88 nm lines. The 209.48 nm line should not be used for samples with a high content of Fe. Relative intensities of 231 W lines have been listed and possible interferences discussed [17]. Laser ablation ICP AES was reported to give a DL of 2 $\mu\text{g g}^{-1}$ [18]. Tungsten is usually determined on preconcentration [10,11].

Mass spectrometry

Tungsten has five stable isotopes, ^{180}W , ^{182}W , ^{183}W , ^{184}W and ^{186}W , with relative abundances of 0.12%, 26.31%, 14.28%, 30.64% and 28.64%, respectively. The most abundant ^{184}W is used for quantification whereas ^{182}W is used as a spike for ID ICP MS [9]. Inductively coupled plasma MS offers a DL of 0.05 ng ml^{-1} . An ADL of 0.5 pg was reported for ETV ICP MS. Two distinct vaporization processes resulting in two separate ETV ICP MS peaks for tungsten have been observed [17]. Chemical modifiers (NaCl, NaF, Freon) were ineffective in preventing the memory effect owing to the formation of tungsten carbide [19,20].

Neutron activation analysis

Neutron activation analysis is based on either the long lived ^{185}W ($t_{1/2} = 73$ d) or short lived ^{187}W ($t_{1/2} = 24$ h, $E_{\gamma} = 840$ keV) [13]. Chemical separation must be employed because of the low γ -ray energies and consequent interferences from other nuclides in the activated sample. An ADL of a few pg can be obtained with RNAA [8,21].

62.2 ANALYSIS OF REAL SAMPLES

Radiochemical NAA and ICP MS are the only techniques able to cope with trace levels of W. Tungsten was determined in environmental waters by ICP MS after preconcentration by sorption [12]. Rocks and ores are usually decomposed by oxidative alkaline [7,9,10] or pyrosulphate [3,16] fusion. The charcoal and flux contributed a blank of $0.3 \mu\text{g g}^{-1}$ [9]. Biological tissues show a W content in the low ppb range and have so far not been widely investigated. Analytical methods for the trace determination of W are summarized in Table 62.1.

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TABLE 62.1

Analytical methods for the determination of trace tungsten

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
River water (0.1 l)	none	sorption on activated charcoal	ICP AES, ICP MS	0.001	11
Spring water (1 l)	none	sorption as W(V)-SCN complex on XAD-7	VIS	n.g.	22
GeoCRMs (0.2 g)	fusion with Na_2CO_3 - NaNO_3	sorption of the W-oxinate complex on charcoal	ID ICP MS ICP AES	0.1	9, 10
GeoCRMs (1 g)	HF	extrn. with dithiol (heptane)	VIS	0.5	12
GeoCRMs (0.1–1 g)	HNO_3 , HF (microwave assisted)	extrn. with BPHA (CHCl_3)	ICP MS	0.08 ^a	4
Ores (0.5 g)	fusion with Na_2CO_3	anion exchange	VIS	1350 ^a	13
Plants, bio-CRMs (0.1 g)	HNO_3 - HClO_4 , H_2O_2	sorption on α -benzoinoxime loaded resin	RNAA	0.003	8
Alloys, concentrates, rocks	H_3PO_4 - HCl - HNO_3 H_3PO_4 - HF - HCl - HNO_3 HNO_3 - HF - HClO_4 or fusion with LiBO_2	n.g.	ICP AES	0.17	17
Animal, plant tissue	n.g.	extrn. with <i>N</i> -p-methoxyphenyl-2-furalacrylohydroxamic acid (MIBK)	FAAS	0.004	15

^a In the solution fed, ng/ml.

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Uranium

Uranium (U, atomic weight 238.04, melting point 1132°C, $d = 18.95 \text{ g cm}^{-3}$) is a silvery white, fairly soft metal. Uranium is a natural radioactive element. It occurs in the earth's crust with an average abundance of 2.4 ppm. Uranium dissolves in dilute acids and alkalis in the presence of an oxidant, e.g. H_2O_2 , and in hot concentrated acids. The most common valence states of U are IV and VI, the latter being more stable. Uranium(IV) is stable in strongly acidic solutions as the green U^{4+} cation and behaves similarly to Th. Uranium(VI) is found in acidic solutions ($\text{pH} < 2.5$) as the yellow uranyl ion, UO_2^{2+} , which tends to hydrolyze in less acidic media. The hydroxide, $\text{UO}_2(\text{OH})_2$, which precipitates above pH 4, is amphoteric. Uranium(VI) forms peroxide, fluoride, tartrate, citrate, carbonate and nitrate complexes. Metals and strong reductants reduce U(VI) to U(IV) in dilute H_2SO_4 .

63.1 SEPARATION AND PRECONCENTRATION

Extraction, coprecipitation and ion-exchange are all used for the separation–preconcentration of U, usually as U(VI). Combined procedures (older than 1985) for the separation of U have been discussed [1].

Extraction

Uranium(VI) can be selectively extracted from a nitrate medium with *O*-donor reagents (MIBK, ethyl acetate, mesityl oxide, TBP, TOPO) [2–4]. The acidity is kept at 0.1–1 M; otherwise, other metals are significantly coextracted. Uranium(VI) can be extracted from HCl, H_3PO_4 or H_2SO_4 with high molecular weight amines into non-polar solvents [5,6]. Many chelating agents have been reported but the selec-

tivity is generally poor [7–13]. Interferences, such as Al or Fe(III), can often be removed by masking with EDTA but excess of EDTA can inhibit the extraction of U [8]. Back-extraction with HNO_3 [7,10] or HCl [8] increases the selectivity. Supercritical fluid extraction with fluorinated β -diketones and TBP has been developed [14].

Coprecipitation

Uranium(IV) can be separated from U(VI) by precipitation as the fluoride UF_4 with La and Ce as collectors [15]. Uranium(IV and VI) is precipitated with $\text{Fe}(\text{OH})_3$ as collector [16,17]. Electrodeposition of U on a stainless steel disk from alkaline solutions and TBP is the end step of α -spectrometric procedures [18].

Sorption and chromatographic techniques

Sorption on cryptomelane-type $\text{MnO}_2(\text{aq})$ [19], TBP-loaded polyurethane foam [20] and various chelating resins [21–23] has been used for preconcentration of UO_2^{2+} . Unlike most metals U(VI) does not form a stable complex with EDTA and is retained on strong cation exchangers from EDTA solutions. Anionic nitrate, sulphate, carbonate and oxalate complexes are used to retain U on anion exchangers. Ion-exchange procedures (often multistep) are commonly used for uranium purification for TI MS [24] and α -spectrometry [3,16]. Volatile U complexes with β -diketones can be separated by GC [25].

63.2 DETERMINATION TECHNIQUES

There exist many instrumental techniques for trace U determination, ICP MS being the most popular. A comparison study of TI MS, INAA and XRF has been published [26].

Spectrophotometry and spectrofluorimetry

The best sensitivity ($\epsilon = 1.27 \times 10^5$ at 665 nm) and selectivity (only Th and Zr interfere) is obtained by the reaction of U(IV) with Arsenazo III in 6–8 HCl [9,21,25]. Uranium (VI) is reduced with granular Zn or Bi or dithionite. The determination is usually preceded by extraction of U from nitrate media. Uranyl ions fluoresce in aqueous solution under UV radiation, especially in the presence of PO_4^{3-} . Under proper conditions 0.1 ng of U can be detected but the method is subject to interferences. Time-resolved laser-induced fluorescence has been proposed for speciation of U ions [27].

Atomic absorption spectrometry

Attempts to determine U by FAAS have been reviewed [28]. The analysis is hampered by the low atomization yield due to the formation of refractory oxides [29]. An $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame and measurements at the 358.5 nm line have been recommended [7]. The poor DL of $120\text{ }\mu\text{g ml}^{-1}$ in aqueous media can be improved by extraction with MIBK [7]. Indirect determination of U by FI and air- C_2H_2 flame has been proposed alternatively [28]. Graphite furnace AAS offers an ADL of 20–50 ng [28]. Use of pyrolytically coated tubes is essential [30].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES suffers from interferences and poor sensitivity (DL of $50\text{--}100\text{ ng ml}^{-1}$) [8]. The 409.014 nm line shows an intensity *ca* 15% lower than that of the 385.958 nm line but shows better background characteristics. The 367.0 ICP line is an alternative [1]. The determination in organic solvents has been evaluated and a DL of $0.35\text{--}0.5\text{ ng ml}^{-1}$ in xylene was achieved [31]. The organic phase is seldom fed into the plasma [13]; U is rather back-extracted into HNO_3 [9] or taken up into aqueous solution after solvent evaporation [1].

Mass spectrometry

Uranium has three natural isotopes ^{238}U , ^{235}U and ^{234}U with relative isotopic abundances of 99.274%, 0.72% and 0.006%, respectively. The most abundant ^{238}U nuclide is free from isobaric overlaps and is used for quantification of the total U. The TI MS determination of ^{238}U and ^{234}U (and isotopic ratio) is based on ID quantification using a double spike ($^{233}\text{U}\text{--}^{235}\text{U}$ [26] or $^{233}\text{U}\text{--}^{236}\text{U}$ [24]) to correct for mass fractionation. The DLs are at the 1–2 ng level for ^{238}U and 10–20 ng for ^{234}U [24]. Inductively coupled plasma MS offers a DL at the 1 pg ml^{-1} level [32,33]. ^{205}Tl and ^{209}Bi are used as internal standards [2,34]. In the ID mode ^{235}U [35–37] and ^{236}U [32] have been used as the spike. The mass discrimination between ^{235}U and ^{238}U was 2.5% per dalton [32]. If ^{235}U is used a further correction for the 0.72% natural abundance must be applied which is not necessary in the case of ^{236}U (absent in real samples) [32]. Formation of U hydride under ICP MS conditions has been studied [38]. Optimization of ICP MS conditions for U has been discussed in detail [39].

Neutron activation analysis

Instrumental NAA is based on counting the ^{239}U ($t_{1/2} = 23.5\text{ min}$) photopeak ($E_\gamma = 74\text{ keV}$) produced by the $^{238}\text{U}(\text{n},\gamma)^{239}\text{U}$ reaction after

short irradiation [11]. For RNAA the ^{239}Np nuclide ($t_{1/2} = 2.35$ d, $E_{\gamma} = 277$ keV) produced in the reaction $^{238}\text{U}(n,\gamma)^{239}\text{U} \xrightarrow{\beta^-} ^{239}\text{Np}$ is used but long irradiation and cooling times are required [40,41].

α -Spectrometry

α -Spectrometry coupled with solvent extraction and anion-exchange separation and electroplating requires large sample weights owing to low activities. An ADL of 15–30 ng is readily achieved [16,42].

Miscellaneous

Energy-dispersive XRF of uranium collected on the filters [43] or from evaporated extracts [12,44] has been reported. Direct determinations of U by time-resolved laser induced spectrometry (DL 0.2 ppm) [45] and by thermal lensing spectrophotometry (DL down to pM level) [46] have been proposed. Uranium complexes with fluorinated chelating agents can be detected by ECD after GC separation [25].

63.3 ANALYSIS OF REAL SAMPLES

Natural waters

Uranium is fairly soluble in oxygenated seawater where its concentration (1–3 ppb) exceeds by a decade that in fresh waters (0.1 ppb) [47]. Uranium exists mainly as U(VI) carbonate complex $\text{UO}_2(\text{CO}_3)_2^{2-}$, but stable U complexes with organic matter (humic and fulvic acids) are known [22,48]. Ultraviolet cleavage (in the presence of H_2O_2 under acidic conditions) is recommended [17,22], otherwise differences in sorption and extraction behaviour from sample to sample are expected. Speciation of uranium in seawater (inorganic, weakly bound, strongly bound) has been discussed [22]. Fractional determination of U(IV) and U(VI) by selective extraction with *N*-cinnamoyl-*N*-(2,3-xylyl)hydroxylamine into toluene and catalytic determination using the oxidative coupling of 4-aminoantipyrine with *N,N*-dimethylaniline has been developed [49]. α -Spectrometry has been widely used for the determination of the total U and the $^{234}\text{U}/^{238}\text{U}$ ratio but samples of ca 10 l are required. Thermal ionization MS can be routinely applied to ca 10 ml of seawater (for ^{234}U and 1 ml for ^{238}U [24]. ICP MS can be in principle applied to direct analysis of river water with an ultrasonic nebulizer [33]. The direct determination and that after coprecipitation with $\text{Fe}(\text{OH})_3$ have been compared [33]. NAA was widely applied to the analysis of natural waters [48,50,51]. Combined procedures for the determination of U in natural waters are summarized in Table 63.1.

TABLE 63.1

Methods for the determination of uranium in natural waters

Water (amount)	Separation and/or preconcentration	Detection	DL (ng/ml)	Ref.
Natural (1l)	sorption on TBP-loaded polyurethane foam	VIS	0.05	20, 52
Natural (n.g.)	extraction with <i>N-p</i> -methoxyphenyl-2-furylacrylohydroxamic acid (CHCl ₃ and MIBK)	VIS, FAAS	5–6	7
Sea (0.2 l), tap (0.5 l)	coprecipitation with PAN	INAA	0.004	48
Sea (1 ml)	anion exchange	TI MS	2	24
Sea (3 ml)	anion exchange, coprecipitation with Fe(OH) ₃ , anion exchange	TI MS		24
Pore, sea, river (0.25 ml)	20-fold dilution	ID ICP MS	0.04	32
Spring (5 l)	evaporation, coprecipitation with Fe(OH) ₃ , anion exchange, electroplating	α-spec	n.g.	17
Pore (1 ml)	anion exchange, coprecipitation with Fe(OH) ₃ , anion exchange, electrodeposition	α-spec	0.0003	16
Mine (4 ml), soil (0.1 g)	SFE with TTA–TBP	RNAA	n.g.	14
Waste (200 ml)	sorption on a chelate fibre; desorption with HNO ₃	ICP AES	5	51

Rocks, soils, sediments and biota

A knowledge of the migration mechanism of U is essential to elucidate nuclear reactions in geochemical processes and the behaviour of nuclear waste repositories. Gas-phase dissolution (with nitric oxide or hydrogen chloride) for remote sample preparation for the determination of U in soils has been developed; the method is suitable for remote dissolution of samples in particularly harsh (e.g. radioactive) environ-

ments [53]. Geochemistry of U in the marine environment has been discussed [16]. Speciation of particulate U based on sequential leaching with (1) 0.05 M acetate buffer (pH 4.0) for labile complexes (hydroxides, carbonates, silicates), (2) 0.01 M HCl for $\text{U}(\text{OH})_4$, oxalate and other organic complexes, (3) 0.1 M HCl (U-EDTA complexes), and (4) HNO_3 -HCl attack for lattice-held uranium has been developed [54]. In air particulate dust and soil U is determined directly on acid digestion by ICP MS [39]. The uranium content in biomaterials is below 0.1 ppm. Direct ICP MS in plant, animal and bone tissue, human lung after dry ashing [34,39,55] or wet digestion [39,56] has been reported. Analytical methods for the determination of U in ecological samples are summarized in Table 63.2.

Clinical samples

Levels of U in human tissues [59] and urine [60] have been summarized. Uranium was found to be below 20 pg ml^{-1} by direct ICP MS [61] and kinetic laser phosphorescence was able to determine U in urine [62].

Industrial materials

Uranium is an α -emitter and can spoil characteristics of high performance electronic devices. Instrumental NAA, GD MS and ICP MS have been compared for the analysis of high purity aluminium [3]. Instrumental NAA gives a DL of 7 ng g^{-1} which decreases to 0.3 ng g^{-1} upon removal of ^{24}Na (on Sb_2O_5) [63] and, further to 0.05 ng g^{-1} by a two-step cation exchange [64]. ICP MS in CF nebulization mode is not sufficient for the sub-ng/g determination level but LA ICP MS proved to be successful [65]. Ion interaction HPLC with *on-line* ETA AAS detection has been used for speciation of U(IV) and U(VI) in solid salts [66]. Analytical methods for the determination of U in industrial materials are summarized in Table 63.3.

Quality control and assurance

Detection limits are blank controlled at the sub-nanogram level [24]. There exist series of NBS standards for U isotopic ratio, SRM 960 and SRM 950a. Certified reference materials for U have been discussed [70]. The 612-617 NIST CRM glasses are available with certified sub- $\mu\text{g/g}$ to $\mu\text{g/g}$ contents of U. For natural materials see tables in Part II.

TABLE 63.2

Determination of uranium in environmental and biological materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL	Ref.
Sediment (1 g)	HF-HCl-HNO ₃	anion exchange, copptn. on Fe(OH) ₃ , anion exchange, electrodeposition	α-spec	0.3 ng/kg	16
Coal ash (0.5 g)	HF-HNO ₃ , HClO ₄ -HNO ₃	extrn. with TTA (benzene), back extrn. (HNO ₃)	ICP AES	30 ng/ml	8
Soil (0.5 g)	HF-HNO ₃ -HClO ₄	on-line sorption on a chelating resin	ICP MS*	0.003 ng/g	23
Soil (<50 g)	ashing, leaching: HNO ₃ , HF, Al(NO ₃) ₂	extrn. with TOPO, back. extrn. (NH ₄ F), copptn. with LaF ₃ , electroplating	α-spec	2 mBq	57
Apatite (0.1-0.2 g)	HNO ₃	extrn. with 3-phenyl-4-benzoyl-5-isoxazolone (DIBK)	ICP AES	20 ng/ml	13
CRM plants, bone (0.5 g)	ashing, HCl, HF-H ₂ O ₂ ; for bone: HClO ₄ -HNO ₃	copptn. with PAN	INAA	5 µg/kg	48
CRM diet	HNO ₃	anion exchange; copptn. of Np with BaSO ₄	RNAA	0.2 ng	58
Plant, animal tissues (n.g.)	H ₂ SO ₄ -HNO ₃ , H ₂ O ₂	extrn. with <i>N</i> - <i>p</i> -methoxyphenyl-2-furylacrylohydroxamic acid (CHCl ₃ and MIBK)	VIS, FAAS	5-6 ng/ml	7
Geosamples (1 g); CRM animal bone (1 g)	geo: HNO ₃ -H ₂ SO ₄ bone: HNO ₃ -HClO ₄	extrn. with DB-24-crown-8 (PhNO ₂); back extrn. HNO ₃	VIS	n.g.	10

FOD = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione; * detection of ²³⁴U.

TABLE 63.3

Determination of uranium in industrial materials

Sample (amount)	Decomposition	Separation and/or preconcentration	Detection	DL (ng/g)	Ref.
Glass (500 mg)	HF	volatn. of the matrix as SiF_4 , BF_3	ICP MS	1	25
Glass (500 mg)	HClO_4 -HF- H_3BO_3	volatn. of the matrix as SiF_4 , BF_3 ; sepn. of Zr by extrn. with TTA, extrn. of U with TTA-TBP	VIS	20	9, 25
Glass (5 g)	HClO_4 -HF- H_3BO_3	extrn. with FOD-TBP (toluene), GC	ECD	1000	25
Aluminium (1-5 g)	HNO_3 -HCl	see in the text	ICP MS	few	3
Aluminium (0.1 g)	HCl	ion-exc. see text	RNAA	0.05	64
Aluminium (10 g)	HCl (Cu catalyst)- H_2O_2	extrn. with TBP (cyclohexane), back extrn. H_2O	ICP MS	0.007	2
Aluminium (3g)	HNO_3	anion exchange of ^{239}Np	RNAA	0.0005	67
Aluminum (10 g)	HNO_3	extrn with TOPO (CHCl_3); evapn.	ICP AES	12	1
Polyimide, SiC, aluminium oxide	HF- HNO_3 (bomb); HCl (bomb) (Al_2O_3)	anion exchange	RNAA	0.01-0.1	41
Zr alloy (1 g)	HF- HNO_3	extrn. into MIBK	ID ICP MS		37
W metal (0.1 g)	HF- HNO_3	anion exchange	RNAA	4	68
Ta metal	HF	cation exchange	RNAA	n.g.	69
MoO_3/WO_3 (50 g)	NaOH	sorption on Hyphan, extrn. with TAO or <i>n</i> -butylaniline (CHCl_3); back extrn.	VIS	3-20	21

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Vanadium

Vanadium (atomic weight 50.94, melting point 1890°C, $d = 6.11 \text{ g cm}^{-3}$) is a silvery grey metal. It occurs in the earth's crust with an average abundance of 0.01%, primarily in fossil fuels as a porphyrin complex. The metal dissolves in concentrated H_2SO_4 , HNO_3 and HF . In aqueous solutions V can exist in II, III, IV and V oxidation states, the most stable of which are IV and V. Vanadium (IV) is produced by the dissolution of V_2O_5 in HCl and occurs as the blue, VO^{2+} ion, stable in acidic media and readily oxidized to V(V) in alkaline solutions. Vanadium (V) occurs as VO_2^+ (vanadyl) and VO_4^{3-} (vanadate) in acid and alkaline media, respectively. Vanadyl hydroxide, $\text{VO}(\text{OH})_2$ precipitates at pH ~4 and is amphoteric. Vanadium (IV) forms fluoride, oxalate, EDTA and peroxide complexes. Vanadium (V) forms peroxide complexes and heteropolyacids with P(V), Mo(VI) and W(VI). The demand for trace level determination of V occurs primarily in ecotoxicology (release of V due to the combustion of oil) and clinical chemistry (traces of V are considered essential for cell growth) [1].

64.1 SEPARATION AND PRECONCENTRATION

Controlling the valence of V in aqueous solution is the major problem. Vanadium is usually oxidized to V(V) prior to extraction, e.g. with KMnO_4 or $\text{K}_2\text{S}_2\text{O}_8$ or by oxidative digestion [2–4]. Separation of V(IV) from V(V) has been exhaustively reviewed [5].

Extraction

Vanadium (V) is efficiently separated by extraction with 8-hydroxyquinoline at pH 3–3.5 by CHCl_3 or MIBK followed by stripping at pH

9.4 [6,7]. Extraction of V(V) with BPHA or its derivatives from strong acid media, usually into CHCl_3 , is an attractive alternative [2–4,8]. Cupferron extracts V into CHCl_3 at pH 1.0–2.0 [9,10].

Coprecipitation

Coprecipitation of $\text{VO}_2(\text{OH})$ with $\text{Fe}(\text{OH})_3$ or In-loaded cellulose at pH 6 as collectors is possible [11]. Selective, pH-controlled precipitation of V(V) (pH 1.8) and V(IV) (pH 4) with DDTC has been reported [12].

Sorption

Sorption of V(V) 8-hydroxyquinoline [13,14] and DTC [15,16] complexes on activated carbon or polymeric resins has been reported. Vanadium(IV and V) is retained from acid media on strong cation exchangers. From basic media vanadate is retained on a strong anion exchanger while V(IV) is eluted as VO^{2+} [17]. Vanadium(V) is retained on ethylenediamine bonded silica [18] and on chelating resins [19–21]. Vanadium can be eluted with NH_3aq [21] but digestion of the resin may be necessary to recover the element [20].

Chromatographic techniques

Vanadium porphyrins are sufficiently volatile and thermally stable to be separated by high-temperature GC [22–24]. Other techniques include reversed-phase [25–27] and size-exclusion [25,28,29] chromatography. Reversed-phase chromatography was used to separate V as the complex with PAR [30] or 5-Br-PADAP [8,31] from many metals. The V(V)–BPHA complex was separated by normal-phase HPLC [8].

64.2 DETERMINATION TECHNIQUES

Spectrophotometry

Spectrophotometry of V(IV and V) has been comprehensively reviewed [5]. The measurement of the absorbance of extracts of the V(V)–8-hydroxyquinolinolate and V(V)–BPHA complexes forms the basis of selective but poorly sensitive methods. A better sensitivity can be obtained with PAR ($\epsilon = 3.6 \times 10^4$ at 525 nm) but a prior separation of V is necessary [30]. Sensitivity can be improved by ion pairing of the V(V)–3,5-dinitrocatechol complex with basic dyes ($\epsilon \sim 2 \times 10^5$) [32,33]. The determination of V(V) based on its catalytic effect on various reactions is exceptionally sensitive (DL 0.05 ng ml^{-1}) but nonselective [34,35].

Flame atomic absorption spectrometry

Flame AAS offers a sensitivity of *ca* 2 $\mu\text{g ml}^{-1}$ in the recommended $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ reducing (rich, red) flame at the most intensive 318.4 nm line (actually a triplet: 318.3/318.4/318.5). Ionization should be controlled by the addition of an alkali metal salt (e.g. KCl). Excess of Mg, Ca, Fe, Al, Ti and H_3PO_4 enhances the V signal [14].

Graphite furnace atomic absorption spectrometry

Graphite furnace AAS offers an ADL of 5–50 pg (DL 0.1–1 ng ml^{-1}) [10,36,37]. Factors influencing the atomization of V have been discussed [38]. The major problem is the formation of a refractory carbide by the reaction of V with the graphite of uncoated tubes which is especially troublesome in the presence of La, Mo, W and Zr [38,39]. Pyrolytically coated tubes [36–40] and maximum power heating [38,39] are required. Halogens prevent carbide formation and injection of chlorine was used to abolish carry over [41]. Ashing temperatures are not critical owing to the low volatility of V [39]. Pre-heating of the tube (hot injection) was found to improve results [6,42]. Magnesium nitrate has been recommended as the general purpose matrix modifier [38,39] but $\text{Pd}(\text{NO}_3)_2$ [39] and $\text{Cr}(\text{NO}_3)_3$ [40] were found to be better in particular cases. Background correction is essential [39].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 2–5 ng ml^{-1} at the recommended 292.40 nm line. Iron and Ni overlap making separation necessary [4,18–20,43].

Mass spectrometry

Vanadium has two stable isotopes: ^{50}V (0.25%) and ^{51}V (99.75%) and is readily amenable to TI MS [14,21,25]; the ^{51}V nuclide is used for quantification and the ^{50}V one is the spike [21]. The ^{50}Cr and ^{50}Ti nuclides overlap with ^{50}V and corrections based on the known natural isotopic abundances are required [21]. In ICP MS ^{51}V is overlapped with $^{35}\text{Cl}^{16}\text{O}^+$. This interference was removed by the addition of N_2 to the nebulizer Ar gas [44,45], anion exchange [46], or conversion of Cl^- to HCl and cryodesolvation [47,48]. Addition of 2% H_2 to the aerosol gas enhanced the signal by a factor of 2–3 [47].

Neutron activation analysis

Neutron activation analysis is based on the reaction: $^{51}\text{V}(\text{n},\gamma)^{52}\text{V}$ and counting the short lived ^{52}V ($t_{1/2} = 3.78$ min, $E_\gamma = 1.434$ MeV). An ADL of 0.4 ng can be achieved [9]. Because of the short lifetime radiochemical

separation is hardly possible unless by rapid one-step extraction [3,9]. Instrumental NAA following the pre-separation by sorption is usually applied [15,49].

X-ray fluorescence

Wavelength-dispersive XRF in fuel and residual oils offers a DL of $0.08 \mu\text{g g}^{-1}$ [50]. Energy-dispersive XRF determination of V is interfered with by Fe and Ti spectral overlaps and the strong background continuum in the V fluorescence region [51]. A cobalt anode X-ray tube was shown to overcome many of these problems [51,52]. Alternatively, V(V) and V(IV) can be selectively precipitated with DDTC prior to ED XRF [12].

64.3 ANALYSIS OF REAL SAMPLES

Vanadium is often determined in a multielement array and many procedures including this element are reported in tables in Part II.

Water

Natural waters contain V(V) and V(IV) at similar concentration levels [18]. In oxygenated seawater V is predicted to occur as V(V), primarily as anionic species: HVO_4^{2-} , H_2VO_4^- and NaHVO_4^- , and is not able to form stable complexes with major seawater ligands [15,53]. Because of the complex and unknown speciation direct analysis is preferred. A DL of 0.27 ng ml^{-1} has been reported for GF AAS of mineral water [36]. Direct ICP MS offers DLs of 0.01 ng ml^{-1} , 0.15 ng ml^{-1} and 0.5 ng ml^{-1} for river water, estuarine water and seawater, respectively [47]. Analytical methods involving preconcentration steps are summarized in Table 64.1.

Clinical materials

About 95% of V in blood is bound to transferrin in plasma erythrocytes [37]. Factors affecting the analysis of human serum have been the subject of a chemometric study [55]. Avoidance of stainless steel equipment and working under class 100 conditions are required [37]. Serum is usually decomposed and an extraction separation–preconcentration step is applied. Slow evaporation of urine with HNO_3 gave rise to losses of V [7]. Urine can be analyzed directly [10] or upon dilution (2+1) with 2% HNO_3 –0.001% Triton X-100 [37] with Zeeman correction with a DL of $0.1\text{--}1 \text{ ng ml}^{-1}$. Injection of urine extract on a pre-heated (150°C) graphite

TABLE 64.1

Analytical methods for the determination of total vanadium in water

Water (amount)	Separation/ preconcentration	Detection	DL (ng/ml)	Ref.
Sea (1 l)	sorption of APDC complex on charcoal	INAA	0.025	15
Sea (1–2 l)	sorption on Chelex-100, digestion of the resin	ICP AES	0.25	20
Mineral (10 ml)	extraction with 8-hydroxy-quinoline (MIBK)	GF AAS	0.16	6
Mineral (1 l)	anion exchange as thiocyanate complex, elution with $\text{HClO}_4\text{--HCl}$	ICP AES	0.02	43
River (200 ml)	UV photolysis; coprecipitation of $\text{VO}(\text{OH})_2$ with In-loaded cellulose, stripping with HCl	GF AAS	0.15	11
		ICP AES	0.08	
Sea, river	sorption on ethylenediamine bonded silica [V(V)]; sorption on EDTA-silica [V(V)+V(IV)]	ICP AES	0.06	18
Waste	evaporation, dissolution in HCl--HNO_3 , extraction with caffeic acid–Aliquat 336 (<i>iso</i> -AmOH)	VIS	n.g.	54

tube resulted in a 10-fold increase in sensitivity and improvement in accuracy [42]. Direct ICP MS offers a DL of 1 ng ml^{-1} [44,47]. Combined procedures for the determination of V in clinical samples are summarized in Table 64.2.

Ecological samples

Vanadium(IV) seems more stable under acidic-reduced conditions in soils or sediments where VO_2^+ seems to be complexed by fulvic acids [53]. Care must be taken to ensure that the V species present in the sample match those present in the calibrants [56]. Oxidative soil decomposition or leaching with *aqua regia* and standard addition calibration with V standard solution in HNO_3 has been recommended [56]. Soil leacheates have been analyzed by GF AAS with $\text{Pd}(\text{NO}_3)_2$ as matrix modifier and

TABLE 64.2

Determination of V in clinical materials

Sample (amount)	Decomposition	Separation/preconcentration	Detection	DL (ng/ml)	Ref.
Serum	HNO ₃ -HClO ₄	sorption on Chelex-100, elution with NH ₃ aq	ID TIMS	n.g.	21
Serum (10 ml)	HNO ₃	anion exchange (INAA); extraction with cupferron (CHCl ₃) (RNAA)	INAA, RNAA	0.4 ^a	9
Serum, bioCRMs (<1 g)	HClO ₄ , HNO ₃	extraction with BPHA (toluene)	RNAA	n.g.	3
Serum (4 ml), urine (5 ml)	H ₂ SO ₄ -HNO ₃ -HClO ₄	extraction with <i>N</i> -benzoyl- <i>N</i> -(<i>o</i> -tolyl)-hydroxylamine (benzene)	GF AAS	0.08	2
Urine	evapn. with H ₂ SO ₄	sorption on activated carbon as oxine complex	FAAS	n.g.	13
Urine (5–8 ml)	none	extraction with cupferron (MIBK)	GF AAS	0.05–0.1	7, 42
Urine (25 ml)	evapn.	residue digested with HNO ₃ , extraction with 8-hydroxyquinoline (MIBK)	GF AAS	0.5	5

^a Absolute detection limit, ng.

D₂ background correction [39]. A similar approach is taken for biomaterials. Care must be taken not to lose volatile VOCl₃ (boiling point 126°C) during sample decomposition [57]. The use of HCl for sample dissolution or a high chloride matrix makes it almost impossible to determine ⁵¹V⁺ because of interference from ³⁵Cl¹⁶O⁺ [44]. Direct FAAS of the HNO₃ digest of yeast has been proposed [23]. Combined procedures for the determination of V in biological materials are summarized in Table 64.3.

TABLE 64.3

Determination of vanadium in ecological materials

Sample (amount)	Decomposition	Separation/ preconcentration	Detection	DL	Ref.
Biomaterial (0.5 g)	HNO ₃	anion exchange	INAA	4 ^a	49
Animal tissues, bioCRMs	dry ashing, dissoln. in HNO ₃ –HClO ₄	sorption on activated carbon as oxine complex	FAAS		13
Vegetables (10 g of ash)	HCl–HNO ₃	extraction with caffeic acid–Aliquat 336 (isopentanol)	VIS		54
Vegetables (8–70 g)	dry ashing, dissoln. in HNO ₃ –HClO ₄ or wet: HNO ₃ –HClO ₄	sorption of the oxine complex on charcoal	FAAS	3.0 ^b	14
Citrus leaves (2–3 g)	HNO ₃ –HClO ₄	cation exchange, sorption on Chelex-100, eln. with NH ₃ aq	ID TIMS	n.g.	21
Clam (0.2–0.4 g)	HNO ₃ , HClO ₄ , HCl	extraction of FeCl ₄ [–] (MIBK), extraction with BPHA (CHCl ₃), HPLC	VIS	1.7 ^b	54
Oyster	HNO ₃ –HF–HClO ₄	cation exchange, sorption on Chelex-100, elution with NH ₃ aq	ID TIMS		18

^a Absolute detection limit, ng; ^b in the solution fed, ng/ml.*Industrial samples*

Vanadium is often determined in steels but rarely at trace levels (*cf.* Section 11.1). A rapid procedure for the determination of V in heavy crude oils by ICP AES has been developed [58]. A direct FAAS method for the determination of V in fuel oils has been developed and its accuracy tested in a round-robin test, independent results obtained in 54 laboratories by NAA, GF AAS, ICP AES, ICP MS and XRF confirmed the applicability of the method to routine analysis [59].

Speciation

The biological activity of V depends on its oxidation state. It is recognized that V(V) as vanadate is more toxic than V(IV) present as vanadyl ions [60]. Analytical methods are usually based on selective separation followed by off-line detection. *On-line* procedures are scarce. The presence of V bound to porphyrins has been enjoying increasing interest with respect to fouling of catalysts. Relevant analytical procedures are summarized in Table 64.4.

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TABLE 64.4

Speciation of vanadium using hyphenated techniques

Species	Sample	Separation (eluent)	Detection	Ref.
V(IV),V(V)	catalysts	leaching with HNO ₃ , reversed-phase HPLC of PAR complexes (MeOH-H ₂ O, acetate buffer)	VIS	30
Porphyrine	crude oils	high temperature capillary GC	MIP AES	24
Porphyrine	coals oil shale	high temperature capillary GC	ICP MS	23
Porphyrine	oil shale	packed column GC	MS	22
Porphyrine	crude oil, gasoline	capillary GC	MIP AES	61
Porphyrine and non-porphyrine complexes	heavy crude petroleums, asphaltenes	RP HPLC (gradient THF-MeOH)	GF AAS	25
Various complexes	petroleum crudes and residua	SEC (aromatic solvents)	ICP AES	28
Various complexes	oil	SEC	ICP AES	62
Porphyrine and non-porphyrine complexes	petroleum crudes, asphaltenes	SEC (THF)	GF AAS	25, 29
Porphyrine	fossil fuels	extraction with toluene-MeOH, CHCl ₃ -MeOH, reversed-phase HPLC (MeOH-CH ₃ CN)	UV/VIS	27
Porphyrine	sediment extracts	reverse-phase HPLC (MeOH-CH ₃ CN)	UV/VIS	26
Macromolecular biocomplexes	natural waters	SEC (phosphate buffer, pH 7.3)	GF AAS ICP AES	63

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Zinc

Zinc (Zn, atomic weight 65.39, melting point 420°C , $d = 7.14 \text{ g cm}^{-3}$) is a bluish-white, rather soft metal. It occurs in the earth's crust with an average abundance of 70 ppm, primarily as sulphide (sphalerite or wurzite). The metal (unless very pure) dissolves readily in HCl , H_2SO_4 , H_3PO_4 or acetic acid with liberation of H_2 . The metal dissolves in strong alkalis to form $\text{Zn}(\text{OH})_4^{2-}$ and H_2 . In aqueous solution, Zn occurs always in oxidation state II. The hydroxide, $\text{Zn}(\text{OH})_2$, begins to precipitate at pH 6.8 and dissolves in excess of alkali or NH_3aq . Powdered zinc reduces chromate, permanganate or nitrate in acid solution. In living organisms Zn is associated with metallothioneins and is considered an essential trace element. The need for trace level Zn determination is particularly acute in clinical analysis.

65.1 ANALYTICAL TECHNIQUES

Separation and preconcentration

Separation and preconcentration of Zn are seldom used because of the serious contamination risk. Sorption on chelating resins, often *on line*, is the usual choice [1–4]. Extraction of the Zn complexes with halides or thiocyanate [5], dithizone [6] or dithiocarbamates [7,8] is an alternative. A high temperature GC method for the separation of Zn from the Al matrix has been proposed [9].

Spectrophotometry

The dithizone method is definitely the most popular owing to its high sensitivity ($\epsilon = 9.3 \times 10^4$ at 538 nm) and selectivity provided that it is carried out at the correct pH and in the presence of appropriate masking

agents. Zinc dithizonate is usually extracted at pH about 5 from the acetate buffer containing tartrate and thiosulphate and the free dithione is stripped from the organic phase (CCl_4) with dilute NH_3aq .

Fluorometric methods

Fluorometric methods are based on the Zn chelates with 8-hydroxyquinoline derivatives [3,10–12] and salicylaldehyde hydrazones [13,14]. The fluorescence is enhanced in micellar media [11,12]. Selectivity is improved by mathematical data treatment [10,14] or by masking the interferents [11–14]. Detection limits reach the low ng/ml level [10–13].

Atomic absorption spectrometry

Both EDLs and HCLs provide similar detection characteristics. Flame AAS offers a sensitivity of $0.02 \mu\text{g ml}^{-1}$ in the recommended air- C_2H_2 (oxidizing, lean, blue) flame at the 213.9 nm line. Graphite furnace AAS offers a characteristic mass of 0.1 pg (DL *ca* 1 pg ml^{-1}) using pyrocoated tubes, platform atomization and the $\text{Mg}(\text{NO}_3)_2$ matrix modifier. The maximum allowable pyrolysis temperature without Zn loss is 700°C . The chloride and nitrate interference has been studied in detail [15,16]. The recommended matrix modifiers included Pd-Mg [17], $\text{NH}_4\text{H}_2\text{PO}_4$ [18] and H_3PO_4 [19]. Sulphate is a common interferent [17]. The high sensitivity of AAS makes solid sampling popular [20,21].

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma AES offers a DL of 2–5 ng ml^{-1} at the most sensitive 213.86, 202.55 and 206.20 nm lines. Nickel and Cu overlap at the 202.55 and 213.86 nm lines so the interfering element correction should be used. The 206.20 and 202.55 nm lines should not be used for samples containing high levels of Cr. The presence of some residual organic matter after sample dissolution did not interfere with the determination of Zn [22]. Direct insertion ICP AES has been proposed [23].

Mass spectrometry

Zinc has five stable isotopes: ^{64}Zn (48.63%), ^{66}Zn (27.9%), ^{67}Zn (4.1%), ^{68}Zn (18.75%) and ^{70}Zn (0.62%). Thermal ionization is seldom practised because of the contamination risk. Inductively coupled plasma MS suffers from severe polyatomic interferences, mainly by sulphur oxides and hydroxides [8,24–27]. As the most abundant ^{64}Zn is interfered with by CaO^+ , PO_2^+ and S_2^+ , ^{68}Zn [24] and ^{66}Zn have been counted alternatively

[25,26]. Anion exchange has been used to eliminate spectral interference due to sulphur and chlorine [27]. Sorption on chelating resin has been used to separate Zn from interfering matrix constituents prior to the ^{70}Zn : ^{68}Zn and ^{68}Zn : ^{67}Zn and ^{68}Zn : ^{66}Zn isotope ratio measurements by ICP MS [2,4]. Determination of femtogram amounts of Zn in individual airborne particles by direct ICP MS has been reported [28].

Neutron activation analysis

The most important are the nuclides ^{65}Zn ($t_{1/2} = 245$ d, $E_\gamma = 1.114$ MeV) and $^{69\text{m}}\text{Zn}$ ($t_{1/2} = 13.8$ h, $E_\gamma = 0.44$ MeV) which offer a similar sensitivity. The former is usually chosen, but the latter is especially suitable for a rapid analysis. A chemical separation from interfering radionuclides (e.g. ^{46}Sc , ^{59}Fe , ^{60}Co) is necessary prior to the ^{65}Zn activity measurement [29,30].

65.2 ANALYSIS OF REAL SAMPLES

The ubiquitous presence of Zn in the environment makes the contamination danger of primary importance in trace analysis. Analytical procedures must be kept as simple as possible and the addition of chemical reagents, other than high purity acids for sample decomposition, should be avoided. Zinc is preferably determined directly, often in a multielement array (*cf.* Part II). Combined analytical procedures for the determination of Zn are summarized in Table 65.1.

Water

Seawater contains $0.003\text{--}0.6$ ng ml $^{-1}$ Zn. A study of the influence of the seawater matrix (various chlorides and nitrates) on the atomization of Zn and results obtained by Zeeman effect GF AAS has been presented; in optimized conditions (matrix modification with oxalic acid) a DL of 60 pg ml $^{-1}$ was achieved [15]. A sensitive FI fluorimetric technique for the shipboard determination of Zn open ocean water after *on-line* preconcentration was reported to offer a DL of 6.5 pg ml $^{-1}$ [3].

Clinical samples

The concentrations of Zn in blood, serum, urine and other body fluids ($1\text{--}10$ $\mu\text{g ml}^{-1}$) are readily determined by AAS after direct aspiration into the flame upon $5\text{--}25$ -fold sample dilution [33–37]. Blood collection tubes have been comprehensively evaluated in terms of the contamina-

TABLE 65.1

Combined procedures for the determination of Zn

Sample (amount)	Decomposition	Separation and/or preconcentration	Determin. technique*	Ref.
Seawater (4.4 ml)	none	sorption on immobilized 8-hydroxyquinoline	FLU	3
Red blood cells, plasma (0.2–0.6 g)	HNO ₃ (bomb)	extraction with APDC (CCl ₄)	ICP MS	8
Serum, faeces	dry ashing, dissoln. in HCl	extraction with DDTC (CCl ₄); back-extraction (HCl)	ICP MS	7
Serum, urine, bioCRMs	HNO ₃ –HClO ₄	removal of Na on Sb ₂ O ₅ ; anion exchange	RNAA	29
Urine (15 ml), milk (1 ml)	urine: HNO ₃ (microwave assisted), milk: dry ashing, dissoln. in HNO ₃	sorption on a chelating resin	ICP MS	2
Urine	HNO ₃ (microwave assisted)	extraction with APDC (CCl ₄)	ICP MS	8
Faeces	dry ashing, dissoln. in HCl	anion exchange, elution with 0.04 M HCl	FAB MS TIMS	31
Food, faeces (0.1–10 g)	dry ashing, dissoln. in HNO ₃	extraction with APDC (CCl ₄)	ICP MS	8
Breast tissue	aqua regia–HClO ₄	extraction with TTA (MIBK)	RNAA	30
Animal blood, tissue	HNO ₃	sorption on 8-hydroxyquinoline immobilized on silica	ETV ICP MS	4
Bismuth (1 g)	HNO ₃	extraction as Zn (SCN) ₄ ²⁻ (MIBK)	ETA AAS	5
Organopalladium compounds (1 g)	HCl	matrix removal by extraction of Pd as Pd(SCN) ₄ ²⁻ (MIBK), extraction of Zn with APDC (MIBK)	FAAS	32

* DLs generally not given in the original works.

tion risk [38]. Calibration with aqueous standards is generally sufficient but in some cases matrix-matched standards have been recommended [39]. Acid digestion of biofluids and soft tissues [37,40,41], also *on-line* microwave assisted [42], is sometimes applied prior to FAAS. Direct solid sampling GF AAS has been reported for milk [20], salivary calculi [43] and bloodstain [44]. GF AAS has been reported for human milk on large dilution with Triton-100 [45] but the matrix modifier increased the risk of contamination [17]. Zinc isotopic ratios in serum and faeces after administration of ^{70}Zn have been determined by ICP MS [7,8] and TI MS [31].

Biological samples

The normal Zn levels in plant and animal tissues are at the tens of ppm level and seldom present analytical difficulties. Flame AAS after acid digestion [46,47] is the usual choice. Flow-injection slurry FAAS analysis of foods has been reported [48]. Dry ashing and wet dissolution procedures for the decomposition of milk samples have been compared in terms of the Zn recovery and the residual carbon content [22]. Without ashing aid zinc losses were observed at high temperatures, especially in the presence of chloride [21].

Speciation

Speciation of Zn associated with thioneins is of the primary concern. Retention of Zn-binding albumin, α_2 -macroglobulin and retinol was observed during ultrafiltration of non-protein-bound zinc through cellulose acetate membranes [18]. Reversed-phase [49–54] and size-exclusion [55–60] chromatographies are the most popular separation techniques. Methods for speciation of Zn are summarized in Table 65.2. Speciation of Zn in plant foodstuffs [67] and in flying ash [68] has been discussed in detail.

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TABLE 65.2

Methods for speciation of Zn

Species determined	Sample	Separation (eluent)	Detection	Ref.
Non-protein bound Zn	human serum	ultrafiltration	GF AAS	18
Porphyrins	coals oil shale	GC	ICP MS	61
Protoporphyrin	blood	IIC (50 mM TBAH, pH 7.5, acetonitrile)	FLU	62
Coporphyrin	blood, plasma	RPC (50 mM K_3PO_4 - CH_3CN (5:1), pH 6.8)	FLU	49
Protoporphyrin	urine	RPC (0.1 M NaH_2PO_4 , THF, pH 5.3)	FLU	50, 51
Protoporphyrin	blood	RPC (0.1 M phosphate, MeOH, THF)	FLU	52
Thioneins	chicken meat	RPC (0.1 M CH_3COONH_4 , 0.1% CF_3COOH , pH 6)	ICP MS	53
Thioneins	mussels	SEC (K_2HPO_4 - KH_2PO_4 buffer, pH 7.5)	ICP AES	55
Thioneins	cyano-bacterium	SEC (0.2 M $(NH_4)_2SO_4$, 0.05 M Tris, 1 mM EDTA, pH 7.5)	ICP MS	56
Thioneins	proteins	SEC (I: 0.06 M Tris-HCl buffer, pH 7.5, 0.05% NaN_3 , II: 0.25 M NaCl, 0.06 M Tris-HCl buffer, pH 7.5, 0.05% NaN_3)	ICP MS	57
Thioneins	mussels	SEC (0.03% NaN_3 , 10 mM Tris-HCl buffer, 0.1 M NaCl, pH 7.0)	UV	58
Macromolecular biocomplexes	natural waters	SEC (16 mM K_2HPO_4 , pH 7.3)	GF AAS, ICP AES	59
Proteins	serum, milk seminal fluid	SEC (0.1 M HEPES, 0.1 M NaCl, pH 7.4)	ICP AES	60
Metabolites of auranofin	urine	AEC (gradient elution with 20 mM Tris, pH 5.5-200 mM Tris)	ICP MS	69

Species determined	Sample	Separation (eluent)	Detection	Ref.
Thioneins	rat and fetal bovine liver	RPC [gradient elution with 50 mM Tris-HCl (pH 7.0) in MeOH]	AAS	54
Thioneins	rat hepatome tissue culture	AEC [gradient elution with 20 mM Tris-HCl (pH 7), 0.02% NaN ₃ -250 mM Tris-HCl (pH 7), 0.02% NaN ₃]	γ-spec	70
Thioneins	soy bean flour extracts	gradient gel, isoelectric focusing electrophoresis	FAAS	63
Proteins	proteins	CZE (Tris-glycine or Tris-tricine)	UV	64
Thioneins	rabbit liver	CZE (Tris-HCl, pH 9.1)	UV	65
Chlorophylls		RPC	UV	66

AEC = anion exchange chromatography; SEC = size-exclusion chromatography; IIC = ion-interaction chromatography; RPC = reverse-phase chromatography; CZE = capillary zone electrophoresis; GC = gas chromatography.

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Zirconium

Zirconium (Zr, atomic weight 91.22, melting point 1852°C, $d = 6.53 \text{ g cm}^{-3}$) is a white lustrous metal. It occurs in the earth's crust with an average abundance of 150–200 ppm, primarily in zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$), always accompanied by a small amount of Hf (*cf.* Chapter 29). The metal dissolves readily in dilute HF, *aqua regia* or hot H_2SO_4 containing a high concentration of $(\text{NH}_4)_2\text{SO}_4$. The only oxidation state of Zr in its compounds is IV. In strongly acidic HNO_3 and HClO_4 solutions the Zr^{4+} and ZrO^{2+} ions exist which tend to hydrolyze at pH 1 and to polymerize at elevated Zr concentration. The hydroxide, $\text{Zr}(\text{OH})_4$, which precipitates at pH 1–2 and is soluble in HCl or HF.

66.1 SEPARATION AND PRECONCENTRATION

The methods discussed below apply to both Zr and Hf unless stated otherwise. The few methods that distinguish between Zr and Hf are based on tiny differences in the stabilities of their citrate, oxalate, thiocyanate, formate and various chelate complexes; those of Hf are generally less stable than those of Zr. Accurate control of the reaction conditions is essential [1–3] (*cf.* Chapter 29).

Coprecipitation

Coprecipitation of Zr with $\text{Fe}(\text{OH})_3$ as carrier can be used for its preconcentration from large amounts of water [4] but also for its separation from the melt matrix on fusion [2,5]. Organic reagents, e.g. cupferron can be used alternatively [6].

Extraction

Extraction of Zr with TTA into xylene from 4–6 M HCl is a convenient method for its separation from many ions [7]. Use of BPHA for extraction

from highly acidic media into inert solvents is an alternative whereas other methods are of limited importance. Zirconium is quantitatively extracted with dicyclohexyl-18-crown-6 in CH_2Cl_2 from HCl [3] but not from HF media [8]. A careful choice of extraction parameters enables the separation of Zr and Hf from each other [3]. Solid-phase extraction of Zr and Hf thiocyanates on a polyurethane foam has been studied [9].

Chromatographic methods

Zirconium is retained by strong cation-exchangers [10] and chelating resins [11]. The fluoride, oxalate, ascorbate, sulphate and formate complexes of Zr and Hf have widely been used for their ion-exchange preconcentration separation from other elements and also from each other [12]. Extraction chromatography with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one has been used for the separation of Hf and Zr [13]. Ion-pair reversed-phase HPLC separation of the Zr complex with Tiron has been reported [14].

66.2 DETERMINATION TECHNIQUES

Spectrophotometry

The reaction of Zr (Hf) with Arsenazo III in strongly acidic media (8–10 M HCl) is the basis of its sensitive ($\epsilon \sim 1.2 \times 10^5$ at 665 nm) and fairly selective determination [Th and U(IV) interfere]. Fluoride and oxalate interfere as well, but sulphate and phosphate may be present. The alternative method, based on the reaction of Zr with Xylenol Orange is less sensitive ($\epsilon = 3.5 \times 10^4$ at 535 nm) and less selective.

Atomic emission spectrometry

Atomic emission spectrometry offers a DL of 3 ng ml^{-1} at the most sensitive 339.2 and 343.82 nm lines. The former may be interfered with by Ar at 339.28 and 339.32 nm. Spectral lines and coincidences have been comprehensively discussed [15]. Zirconium is usually determined after separation [6,12]. Laser ablation ICP AES offered a DL of $3 \mu\text{g g}^{-1}$ [16].

Mass spectrometry

Zirconium has five stable isotopes: ^{90}Zr (51.45%), ^{91}Zr (11.22%), ^{92}Zr (17.15%), ^{94}Zr (17.38%) and ^{96}Zr (2.8%). In TI MS, the Mo-isotopes overlaps on ^{92}Zr , ^{94}Zr and ^{96}Zr masses could not be corrected owing to the instability of the Mo beam [4]. The only ratio that can be measured in ID TIMS is $^{90}\text{Zr}/^{91}\text{Zr}$ and it is impossible to correct for mass fractiona-

tion [4]. Inductively coupled plasma MS offers a detection limit of 0.01 ng ml⁻¹. The most abundant ⁹⁰Zr nuclide is used for quantification [6,11] whereas ⁹¹Zr is used as the spike for isotope dilution [11]. The suppression effect of Al has been eliminated by the separation of Zr [11].

X-Ray fluorescence

X-Ray fluorescence offers a DL of 1–2 µg g⁻¹ [17–20]. The direct determination suffers from the spectral interference from Sr K_{β1} emission at 0.0783 nm [5]. A preliminary separation of Zr is required [5].

Neutron activation analysis

Neutron activation analysis is based on the reaction ⁹⁴Zr(n,γ)⁹⁵Zr and counting the ⁹⁵Zr nuclide (*t*_{1/2} = 64.4 d, E_γ = 724.2, 756.7 keV). The most common interference is the ⁹⁵Zr activity produced by fission of ²³⁵U [21,22]. Instrumental and radiochemical NAA are affected to the same degree and correction needs to be applied. Important interfering nuclides are ¹²⁴Sb and ¹⁵⁴Eu [21].

66.3 ANALYSIS OF REAL SAMPLES

The geochemistry of Zr in the hydrologic cycle is virtually unknown. Dissolved Zr ranges from 1 to 10 ng l⁻¹ and is predicted to occur as Zr(OH)₅⁻ [11]. Polymeric hydrated oxides may be present and spike equilibration may pose a problem [4]. Zirconium is neither biologically essential nor toxic so studies of the biological matrices have been scarce [23]. The most advanced is the analysis of soils and rocks. Fusion with various Li borates, sometimes in the presence of LiF or LiBr as releasing agents, followed by leaching with an HF-containing acid mixture is the most popular method of sample decomposition [5,6]. X-ray fluorescence is the most widely used determination technique [20,21]. Results obtained by INAA, RNAA, ID TI MS, SS MS and ICP MS for Zr in soil and meteorites have been compared [21]. Erroneous values for older certified materials have been indicated [21]. Analytical procedures are summarized in Table 66.1.

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TABLE 66.1

Analytical methods for the determination of zirconium

Material (amount)	Decomposition	Separation and/or preconcentration	Detection	DL ($\mu\text{g/g}$)	Ref.
River, sea water (1 l)	none	coprecipitation with $\text{Fe}(\text{OH})_3$, dissoln. in HCl ; cation exchange	ID MS	n.g.	4
GeoCRMs (0.5–1.0 g)	fusion with $\text{Li}_2\text{B}_4\text{O}_7$, dissoln. in HClO_4 – HF – HNO_3	coprecipitation with $\text{Fe}(\text{OH})_3$	XRF	0.9	5
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. with HCl – HF	pptn. with cupferron	ICP AES	1	6
GeoCRMs	Na_2O_2 – NaOH fusion, dissoln. HCl	coprecipitation with $\text{Fe}(\text{OH})_3$, multistep ion exchange	RNAA	n.g.	2
GeoCRMs (1 g)	fusion with LiBO_2 , dissoln. with HCl – HF	coprecipitation with cupferron	ICP MS	0.04	6
Rocks (n.g.)	HF , HClO_4 , fusion with NaOH	extraction of the Zn^{2+} – ZrF_6^{2-} ion associate, back extraction of Zn	indirect AAS	1	24
Scandium oxide (0.1–0.3 g)	HCl , H_2O_2	extraction chrom. with 1-phenyl-3- methyl-4-benzoyl- pyrazol-5-one	ICP AES	0.14	13

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